

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 978 556 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
09.02.2000 Bulletin 2000/06

(21) Application number: 98870173.6

(22) Date of filing: 03.08.1998

(51) Int. Cl.⁷: C11D 3/00, C11D 3/37,
C11D 3/22, D06M 15/423,
D06M 15/11, D06M 15/61,
D06M 13/463

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant:
THE PROCTER & GAMBLE COMPANY
Cincinnati, Ohio 45202 (US)

(72) Inventors:
• Altmann, Markus W.
1050 Brussels (BE)

• Bernaerts, An, (NMN)
2860 Sint-Katelijne-Waver (BE)
• Goossens, Els, (MNM)
2890 Oppuurs (BE)
• Hubesch, Bruno Albert Jean
3601 Leefdaal (BE)
• Masschelein, Axel, (NMN)
1050 Brussels (BE)

(74) Representative:
Engisch, Gautier et al
BVBA Procter & Gamble Europe SPRL,
Temseleaan 100
1853 Strombeek-Bever (BE)

(54) Wrinkle resistant composition

(57) There is provided a composition as well as a method for treating fabrics in order to improve various properties of fabrics, in particular, wrinkle resistance by means of a cross-linking resin having cationic properties.

EP 0 978 556 A1

Description

Technical field of the invention

- 5 [0001] The present invention relates to fabric care compositions and to a method for treating fabrics in order to improve various properties of fabrics, in particular, wrinkle resistance.

Background of the invention

- 10 [0002] The domestic treatment of fabric is a problem known in the art to the formulator of laundry compositions. Hence, it is well known that alternating cycles of using and laundering fabrics and textiles, such as articles of worn clothing and apparel, will inevitably adversely affect the appearance and integrity of the fabric and textile items so used and laundered. Fabrics and textiles simply wear out over time and with use. Laundering of fabrics and textiles is necessary to remove soils and stains which accumulate therein and thereon during ordinary use. However, the laundering operation itself, over many cycles, can accentuate and contribute to the deterioration of the integrity and the appearance of such fabrics and textiles.

- 15 [0003] One solution for improving the appearance and integrity of the fabric can be found in WO98/04772 which provides the treatment of fabric against fabric creasing by application of a composition comprising a polycarboxylic acid or derivative thereof; and then curing the composition using a domestic process. However, it has been found that, although effective in reducing creasing, the compounds described in this patent still do not effectively bind the cellulosic fibers in rinse application.

- 20 [0004] Accordingly, it is an object of the invention to provide compound and compositions thereof which provide effective deposition on the fabric without being detrimental to the appearance and integrity of the fabric. In particular, it is an object of the invention to provide compound or compositions having effective durable press properties.

- 25 [0005] The durable press problem in industrial field is known in the art. Processes for the industrial durable press treatment of textile fabrics were first introduced in the 1960's and have achieved widespread use since that time. These durable press treatment processes typically involve treating the fibers of the textile fabrics with cross-linking agents. Early durable press processes used formaldehyde as a cross-linking agent which, although effective, was highly odorous and undesirable to the consumer.

- 30 [0006] As a consequence, formaldehyde was replaced by reactive resins such as dimethylol urea (DMU), dimethylol ethylene urea (DMEU), and by modified ethylene urea resins, such as dimethylol dihydroxy ethylene urea (DMDHEU). However, still it is known that the desired increases in the durable press performance through the use of cross-linking agents are sometimes accompanied by undesirable losses in other important fabric properties, such as tensile strength, tear strength, abrasion resistance and fabric hand.

- 35 [0007] Further, solutions obtained from industry are not usually transposable to domestic treatments. Indeed, in industrial processes a strict control over parameters such as pH, electrolyte concentration, water hardness, temperature, etc., is possible whereas in a domestic washing machine, such a high level of control is not possible.

- [0008] Moreover, it has been found that solutions from industry do not effectively bind the cellulosic fibers in domestic rinse application.

- 40 [0009] Domestic durable press treatments require conditions that industrial treatment do not have to fulfill. Hence, for domestic durable treatments, the compounds or compositions thereof need to manifest at least one of the following properties:

- 45 i)-provide a low level of aldehyde; indeed aldehyde based cross-linker technologies are less favoured in domestic process from an environmental and safety standpoint because contrary to industry where the process is controlled, in domestic process the consumer is the only person using the product, thus enabling the possibility of misuse. Further, high levels of aldehyde tends to produce an odour which would deter the consumer from using it again. Thus, it is desired to provide durable processes for use in domestic process which are safe to the consumer and provide a good odour acceptance.

- 50 ii)-provide a low or even no tensile strength loss; again as stated above for i), the control of the process in domestic treatment is less measurable. Further, contrary to industry where the fabrics are treated once, domestic treatment involves repeated usage and thus produce a tensile strength loss. Thus, it is desired to provide durable processes for use in domestic process which provide a low or even no tensile strength loss.

- 55 iii)-be usable at low temperature; indeed in a domestic process, and in particular in a domestic rinse process, it is not practical to rely on high treatment temperatures such as those used in industrial processes, that is of above 40°C. Thus, it is also a further desire of domestic durable press to provide a better performance at these low tem-

peratures; indeed industry usually achieves a better performance by close control of the reaction process and its various parameters involved. In domestic treatment, however, this close control cannot be achieved. Thus, the performance of the durable press process needs mostly to be achieved by use of efficient technology.

iv)-be applicable in rinse applications: in such type of application, easier control of the use of the product is achieved, thereby avoiding misuse. Thus, for domestic treatment, the technology involved in the durable press process needs preferably to be suitable for use in rinse application.
and/or

vi)-not provide stiffness to fabrics. Again, as described for ii), the repeated usage that are involved in domestic treatment may also lead to stiff fabric. Accordingly, it is desired to provide durable press process which reduces such negative.

[0010] In addition to the above, industrial processes use high concentrations of cross-linking agents which is required for industrial scale treatment whilst for domestic treatment a low level is most preferred for economical reasons.

[0011] Accordingly, notwithstanding the advances in the art, there is still a need for an efficient and economical composition which provides effective domestic durable press properties on the treated fabrics.

[0012] It has now been found that the use of specific resin compounds fulfill such a need, and are particularly well suited for rinse application.

Summary of the invention

[0013] The present invention is a composition comprising:

- i)-a fabric softening compound; and
- ii)- a cross-linking resin having the property of being cationic.

[0014] In another aspect of the invention, the present invention relates to a method of treating fabric which comprises the steps of:

- i)-contacting the fabrics with an epichlorohydrin adducts of polyamine resins, polyethyleneimine resins, cationic starch, polydiallyldimethylammonium chloride, and mixtures thereof, and
- ii)- curing the composition.

[0015] In a further aspect of the invention, the present invention relates to a method of treating fabric which comprises the steps of:

- i)-contacting the fabrics with a resin compound or composition as defined herein, and
- ii)- curing the composition using a domestic process.

Detailed description of the invention

[0016] The present invention relates to compositions which provide effective durable press on treated fabrics, especially when treated in rinse application.

I-Cross-linking resin having the property of being cationic

[0017] An essential component of the invention is a cross-linking resin having the property of being cationic. By "cross-linking resin having the property of being cationic", it is meant that the resin is at least partially positively charged. It is not however necessary that the reactive part of the molecule carries the positive charge. Indeed, polymeric resins can be based on positively charged monomers which help the deposition on the fibers. Since the cross-linking resins are cationic, i.e. positively charged, they are deposited and well retained on the negatively charged cellulosic fibers when these resins are added to the final rinse of a laundry process.

[0018] Cross-linking resins having the property of being cationic suitable for use herein are those commonly known as having wet strength in the paper field. At least two mechanisms have been postulated to account for the mechanism by which wet strength resin act. One is that wet strength resins form covalent bonds between adjacent fibers while another is that the wet strength resin places a layer over the hydrogen bonds formed between adjacent paper fibers and thus prevents water from breaking the hydrogen bonds.

[0019] Conventional wet-strength agents suitable for use herein include compounds made of epichlorohydrin adducts of polyamines, polyethylenamines, cationic starches, polydiallyldimethylammonium chloride, and mixtures thereof, amine-aldehyde resins such as melamine-formaldehyde resin, amide-aldehyde resins, and mixtures thereof. For use within the meaning of the present invention, there can also be used materials of the above-mentioned classes of substances which admittedly do not themselves possess any outstanding wet-strength properties but, nevertheless, have the same durable press effect as do the wet-strength agents as described therein.

[0020] Among the class of epichlorohydrin adducts of polyamines, polyethylenamines, cationic starches, polydiallyldimethylammonium chloride, and mixtures thereof, the preferred components are the polymeric amine-epichlorohydrin resins selected from the group consisting of a polyamide-epichlorohydrin (PAE) resin, a polyalkylenepolyamine-epichlorohydrin (PAPAE) resin, and an amine polymer-epichlorohydrin (APE) resin, in which the amine groups have been alkylated with epichlorohydrin to produce a polyamine-epichlorohydrin resin that has azetidinium or epoxide functionality. Preferably, for use herein, the cross-linking resin having cationic properties is a cationic wet strength resin that is produced by reacting a saturated aliphatic dicarboxylic acid containing three to ten carbon atoms with a polyalkylenepolyamine, containing from two to four ethylene groups, two primary amine groups, and one to three secondary amine groups (such as diethylenetriamine, triethylenetetramine and tetraethylenepentamine), to form a poly(aminoamide) having secondary amine groups that are alkylated with epichlorohydrin to form a PAE resin.

[0021] These polyamide/polyamine/epichlorohydrin wet-strength resins are fully described by Carr, Doane, Hamerstrand and Hofreiter, in an article appearing in the Journal of Applied Polymer Science Vol. 17, pp. 721-735 (1973). Such resins are available as KYMENE from Hercules, Inc. A commercial synthesis of such resins from adipic acid, diethylene triamine and epichlorohydrin is described in the Carr et al publication, *ibid.*, and is U.S. Pat. No. 2,926,154 (Feb. 23, 1960) to G. I. Keim or US 4,240,995. Reference can be made to these publications for further details regarding the preparation of polyamide/polyamine/epichlorohydrin resins.

[0022] Most preferred cross-linking resin having cationic properties from this class are the wet strength resin Kymene 557H (available from Hercules Incorporated), in which adipic acid is reacted with diethylenetriamine to form a poly(aminoamide) that is alkylated and crosslinked with epichlorohydrin to form a PAE resin. Still another preferred cross-linking resin having cationic properties made of epichlorohydrin are Luresin-RTM and Etadurin which both are polyamidoamine-epichlorohydrin resins.

[0023] Amine-aldehyde resins are suitable cross-linking resins for the present invention and are made by condensation of amine or amide monomers with aldehydes such as formaldehyde or glyoxal. Preferred amines are those having low molecular weight amines e.g. melamine or polymeric amines e.g. poly-diallylamine, preferably quarternized. Preferred amides are those polymeric amides such as polyacrylamide. All these suitable amine/amide monomers can also be copolymerized with cationic monomers.

[0024] Among the class of amine-aldehyde cross-linking resin, preferred are those from the class of melamine-formaldehyde resin. Melamine-formaldehyde resins of this type are known as crosslinking agents of this type in the coating industry and are also described, for example, in German Auslegeschrift Nos. 2,457,387 (U.S. Pat. No. 4,035,213 incorporated herein by reference) and 1,719,324 and, in particular, in U.S. Pat. No. 3,242,230 incorporated herein by reference.

[0025] Preferred melamine-formaldehyde resin are those commercially available under the tradenames Madurit, and Cassurit from Clariant.

[0026] Still other preferred cross-linking resin having the property of being cationic among the class of amine-aldehyde cross-linking resin are the Poly(acrylamide-glyoxal) resin commercially available under the tradename SOLIDURIT KM from Clariant.

[0027] According to the present invention, there can also be used a mixture of wet-strength agents of the above-mentioned types or equivalent compounds.

[0028] Preferably for the purpose of the invention, the cross-linking resin having cationic properties have a molecular weight between 200 and 1,000,000, preferably between 500 and 100,000, most preferably between 1000 and 25,000. Cross-linking resin having a low molecular weight are most preferred for use in the present invention as they are more water-soluble and have a better fiber penetration. By low molecular weight it is meant a molecular weight within the range of from 25 to 2000, preferably from 50 to 1000, and more preferably from 50 to 500.

[0029] The above cross-linking components may be used in a composition for delivery onto fabric, such as by means of a rinse process.

[0030] It is desirable if the level of cross-linking components or derivative thereof is present in an amount of from 0.01 % to 60%, preferably from 0.01 % to 30% by weight of the total composition

[0031] It is advantageous for aldehyde containing cross-linking resins if a catalyst is used with compositions of the invention. Preferred catalysts includes organic acids such as citric acid, succinic acid, and tartaric acids, as well as conventional Lewis acid such as $AlCl_3$ or $MgCl_2$, or salts thereof, or mixtures thereof. A typical example of catalyst is the catalyst NKD made of a mixture of salts and organic acid, and commercially available from Hoechst.

[0032] It is preferred if the level of catalyst is from 10% to 50%, preferably from 20 to 40% by weight of the cross-

linking components or derivative thereof.

[0033] For other cross-linking resins like the Kymene, the use of a catalyst is not necessary.

Fabric softening compound

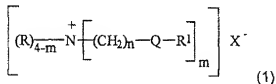
[0034] The composition of the invention also contains a fabric softening compound. Typical levels of incorporation of the softening compound in the composition are of from 1 % to 80% by weight, preferably from 2% to 70%, more preferably from 5% to 60%, by weight of the composition.

[0035] Typical of the cationic softening components are the quaternary ammonium compounds or amine precursors thereof as defined hereinafter.

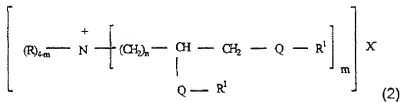
A)-Quaternary Ammonium Fabric Softening Active Compound

[0036]

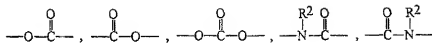
(1) Preferred quaternary ammonium fabric softening active compound have the formula



or the formula:

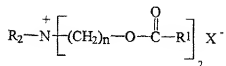


wherein Q is a carbonyl unit having the formula:



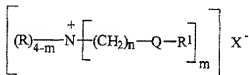
each R unit is independently hydrogen, C₁-C₈ alkyl, C₁-C₈ hydroxyalkyl, and mixtures thereof, preferably methyl or hydroxy alkyl; each R¹ unit is independently linear or branched C₁₁-C₂₂ alkyl, linear or branched C₁₁-C₂₂ alkenyl, and mixtures thereof, R² is hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and mixtures thereof; X is an anion which is compatible with fabric softener actives and adjunct ingredients; the index m is from 1 to 4, preferably 2; the index n is from 1 to 4, preferably 2.

[0037] An example of a preferred fabric softener active is a mixture of quaternized amines having the formula:

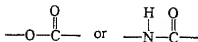


wherein R is preferably methyl; R¹ is a linear or branched alkyl or alkenyl chain comprising at least 11 atoms, preferably at least 15 atoms. In the above fabric softener example, the unit -O₂CR¹ represents a fatty acyl unit which is typically derived from a triglyceride source. The triglyceride source is preferably derived from tallow, partially hydrogenated tallow, lard, partially hydrogenated lard, vegetable oils and/or partially hydrogenated vegetable oils, such as, canola oil, safflower oil, peanut oil, sunflower oil, corn oil, soybean oil, tall oil, rice bran oil, etc. and mixtures of these oils.

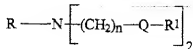
[0038] The preferred fabric softening actives of the present invention are the Diester and/or Diamide Quaternary Ammonium (DEQA) compounds, the diesters and diamides having the formula:



wherein R, R¹, X, and n are the same as defined herein above for formulas (1) and (2), and Q has the formula:

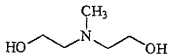


[0039] These preferred fabric softening actives are formed from the reaction of an amine with a fatty acyl unit to form an amine intermediate having the formula:

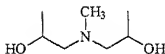


wherein R is preferably methyl, Q and R¹ are as defined herein before; followed by quaternization to the final softener active.

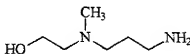
[0040] Non-limiting examples of preferred amines which are used to form the DEQA fabric softening actives according to the present invention include methyl bis(2-hydroxyethyl)amine having the formula:



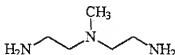
methyl bis(2-hydroxypropyl)amine having the formula:



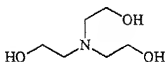
methyl (3-aminopropyl) (2-hydroxyethyl)amine having the formula:



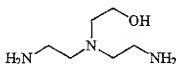
methyl bis(2-aminoethyl)amine having the formula:



triethanol amine having the formula:



di(2-aminoethyl) ethanolamine having the formula:



[0041] The counterion, $X^{(-)}$ above, can be any softener-compatible anion, preferably the anion of a strong acid, for example, chloride, bromide, methylsulfate, ethylsulfate, sulfate, nitrate and the like, more preferably chloride or methyl sulfate. The anion can also, but less preferably, carry a double charge in which case $X^{(-)}$ represents half a group.

[0042] Tallow and canola oil are convenient and inexpensive sources of fatty acyl units which are suitable for use in the present invention as R^1 units. The following are non-limiting examples of quaternary ammonium compounds suitable for use in the compositions of the present invention. The term "tallowyl" as used herein below indicates the R^1 unit is derived from a tallow triglyceride source and is a mixture of fatty alkyl or alkenyl units. Likewise, the use of the term canoly refers to a mixture of fatty alkyl or alkenyl units derived from canola oil.

[0043] In the following table are described non-limiting examples of suitable fabric softener according to the above formula. In this list, the term "oxy" defines a



unit, whereas the term "oxo" defines a -O- unit.

Table II

Fabric Softener Actives

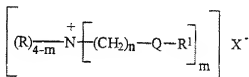
N,N-di(tallowyl-oxy-2-oxo-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride;
 N,N-di(canolyloxy-2-oxo-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride;
 N,N-di(tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
 N,N-di(canolyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride
 N,N,N-tri(tallowyl-oxy-2-oxo-ethyl)-N-methyl ammonium chloride;
 N,N,N-tri(canolyloxy-2-oxo-ethyl)-N-methyl ammonium chloride;
 N-(tallowyloxy-2-oxo-ethyl)-N-(tallowyl)-N,N-dimethyl ammonium chloride;
 N-(canolyloxy-2-oxo-ethyl)-N-(canolyloxy)-N,N-dimethyl ammonium chloride;
 1,2-di(tallowyloxy-oxo)-3-N,N,N-trimethylammonio propane chloride; and
 1,2-di(canolyloxy-oxo)-3-N,N,N-trimethylammonio propane chloride
 and mixtures of the above actives.

[0044] Other examples of quaternary ammonium softening compounds are methylbis(tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate and methylbis(hydrogenated tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate; these materials are available from Witco Chemical Company under the trade names Varisoft® 222 and Varisoft® 110, respectively.

[0045] Particularly preferred is N,N-di(tallowyl-oxy-2-oxo-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride, where the tallow chains are at least partially unsaturated.

[0046] The level of unsaturation contained within the tallow, canola, or other fatty acyl unit chain can be measured by the Iodine Value (IV) of the corresponding fatty acid, which in the present case should preferably be in the range of from 5 to 100 with two categories of compounds being distinguished, having a IV below or above 25.

[0047] Indeed, for compounds having the formula:



derived from tallow fatty acids, when the Iodine Value is from 5 to 25, preferably 15 to 20, it has been found that a *cis/trans* isomer weight ratio greater than about 30/70, preferably greater than about 50/50 and more preferably greater than about 70/30 provides optimal concentration.

For compounds of this type made from tallow fatty acids having a Iodine Value of above 25, the ratio of *cis* to *trans* isomers has been found to be less critical unless very high concentrations are needed.

Other suitable examples of fabric softener actives are derived from fatty acyl groups wherein the terms "tallowyl" and "canoly" in the above examples are replaced by the terms "cocoyl, palmyl, lauryl, oleyl, ricinoleyl, stearyl, palmityl," which correspond to the triglyceride source from which the fatty acyl units are derived. These alternative fatty acyl sources can comprise either fully saturated, or preferably at least partly unsaturated chains.

[0048] As described herein before, R units are preferably methyl, however, suitable fabric softener actives are

described by replacing the term "methyl" in the above examples in Table II with the units "ethyl, ethoxy, propyl, propoxy, isopropyl, butyl, isobutyl and t-butyl."

[0049] The counter ion, X, in the examples of Table II can be suitably replaced by bromide, methylsulfate, formate, sulfate, nitrate, and mixtures thereof. In fact, the anion, X, is merely present as a counterion of the positively charged quaternary ammonium compounds. The scope of this invention is not considered limited to any particular anion.

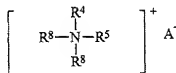
[0050] For the preceding ester fabric softening agents, the pH of the compositions herein is an important parameter of the present invention. Indeed, it influences the stability of the quaternary ammonium or amine precursors compounds, especially in prolonged storage conditions.

[0051] As used herein, when the diester is specified, it will include the monoester that is normally present in manufacture. For softening, under no/low detergent carry-over laundry conditions the percentage of monoester should be as low as possible, preferably no more than about 2.5%. However, under high detergent carry-over conditions, some monoester is preferred. The overall ratios of diester to monoester are from about 100:1 to about 2:1, preferably from about 50:1 to about 5:1, more preferably from about 13:1 to about 8:1. Under high detergent carry-over conditions, the di/monoester ratio is preferably about 11:1. The level of monoester present can be controlled in the manufacturing of the softener compound.

[0052] Mixtures of actives of formula (1) and (2) may also be prepared.

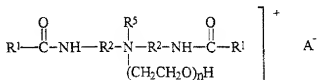
[0053] 2)-Still other suitable quaternary ammonium fabric softening compounds for use herein are cationic nitrogenous salts having two or more long chain acyclic aliphatic C₈-C₂₂ hydrocarbon groups or one said group and an arylalkyl group which can be used either alone or as part of a mixture are selected from the group consisting of:

(i) acyclic quaternary ammonium salts having the formula:



wherein R⁴ is an acyclic aliphatic C₈-C₂₂ hydrocarbon group, R⁵ is a C₁-C₄ saturated alkyl or hydroxyalkyl group, R⁸ is selected from the group consisting of R⁴ and R⁵ groups, and A⁻ is an anion defined as above;

(ii) diamino alkoxylated quaternary ammonium salts having the formula:



wherein n is equal to 1 to about 5, and R¹, R², R⁵ and A⁻ are as defined above;

(iii) mixtures thereof.

[0054] Examples of the above class cationic nitrogenous salts are the well-known dialkyldimethylammonium salts such as ditallowdimethylammonium chloride) ditallowdimethylammonium methylsulfate, di(hydrogenatedtallow)dimethylammonium chloride, distearyldimethylammonium chloride, dibehenyldimethylammonium chloride. Di(hydrogenatedtallow)di methylammonium chloride and ditallowdimethylammonium chloride are preferred. Examples of commercially available dialkyldimethyl ammonium salts usable in the present invention are di(hydrogenatedtallow)dimethylammonium chloride (trade name Adogen[®] 442), ditallowdimethylammonium chloride (trade name Adogen[®] 470, Praepa-gen[®] 3445), distearyl dimethylammonium chloride (trade name Arosurf[®] TA-100), all available from Witco Chemical Company. Dibehenyldimethylammonium chloride is sold under the trade name Kemamine Q-2802C by Humko Chemical Division of Witco Chemical Corporation. Dimethylstearylbenzyl ammonium chloride is sold under the trade names Varisoft[®] SDC by Witco Chemical Company and Ammonyx[®] 490 by Onyx Chemical Company.

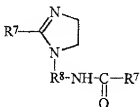
B)-Amine Fabric Softening Active Compound

[0055] Suitable amine fabric softening compounds for use herein, which may be in amine form or cationic form are selected from:

(i)- Reaction products of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof. These reaction products are mixtures of several compounds in view of the multi-functional structure of the polyamines.

The preferred Component (i) is a nitrogenous compound selected from the group consisting of the reaction product mixtures or some selected components of the mixtures.

One preferred component (i) is a compound selected from the group consisting of substituted imidazoline compounds having the formula:

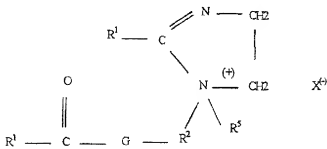


wherein R⁷ is an acyclic aliphatic C₁₅-C₂₁ hydrocarbon group and R⁸ is a divalent C₁-C₃ alkylene group.

Component (i) materials are commercially available as: Mazamide[®] 6, sold by Mazer Chemicals, or Ceranine[®] HC, sold by Sandoz Colors & Chemicals; stearic hydroxyethyl imidazoline sold under the trade names of Alkazine[®] ST by Alkari Chemicals, Inc., or Schercozoline[®] S by Scher Chemicals, Inc.; N,N'-ditallowalkoxydiethylenetriamine; 1-tallowamidoethyl-2-tallowimidazoline (wherein in the preceding structure R¹ is an aliphatic C₁₅-C₁₇ hydrocarbon group and R² is a divalent ethylene group).

Both N,N'-ditallowalkoxydiethylenetriamine and 1-tallow(amidoethyl)-2-tallowimidazoline are reaction products of tallow fatty acids and diethylenetriamine, and are precursors of the cationic fabric softening agent methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate (see "Cationic Surface Active Agents as Fabric Softeners," R. R. Egan, Journal of the American Oil Chemicals' Society, January 1978, pages 118-121). N,N'-ditallow alkoxydiethylenetriamine and 1-tallowamidoethyl-2-tallowimidazoline can be obtained from Witco Chemical Company as experimental chemicals. Methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate is sold by Witco Chemical Company under the tradename Varisoft[®] 475.

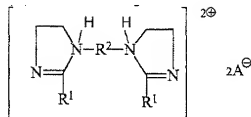
(ii)-softener having the formula:



wherein each R² is a C₁₋₆ alkylene group, preferably an ethylene group; and G is an oxygen atom or an -NR- group; and each R, R¹, R² and R⁵ have the definitions given above and A⁺ has the definitions given above for X⁺.

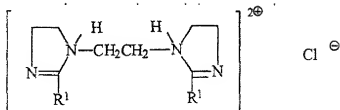
An example of Compound (ii) is 1-oleylamidoethyl-2-oleylimidazolinium chloride wherein R¹ is an acyclic aliphatic C₁₅-C₁₇ hydrocarbon group, R² is an ethylene group, G is a NH group, R⁵ is a methyl group and A⁺ is a chloride anion.

(iii)- softener having the formula:



wherein R, R¹, R², and A⁻ are defined as above.

[0056] An example of Compound (iii) is the compound having the formula:



wherein R¹ is derived from oleic acid.

[0057] Additional fabric softening agents useful herein are described in U.S. Pat. No. 4,661,269, issued April 28, 1987, in the names of Toan Trinh, Errol H. Wahl, Donald M. Swartley, and Ronald L. Hemingway; U.S. Pat. No. 4,439,335, Burns, issued March 27, 1984; and in U.S. Pat. Nos.: 3,861,870, Edwards and Diehl; 4,308,151, Cambre; 3,886,075, Bernardino; 4,233,164, Davis; 4,401,578, Verbruggen; 3,974,076, Wiersma and Rieke; 4,237,016, Rudkin, Clint, and Young; and European Patent Application publication No. 472,178, by Yamamura et al., all of said documents being incorporated herein by reference.

[0058] Of course, the term "softening active" can also encompass mixed softening active agents.

[0059] Preferred among the classes of softener compounds disclosed herein before are the diester or diamido quaternary ammonium fabric softening active compound (DEQA).

[0060] Fully formulated fabric softening compositions may contain, in addition to the hereinbefore described components, one or more of the following ingredients.

OPTIONAL INGREDIENTS

(1) Liquid carrier

[0061] Another optional, but preferred, ingredient is a liquid carrier. The liquid carrier employed in the instant compositions is preferably at least primarily water due to its low cost, relative availability, safety, and environmental compatibility. The level of water in the liquid carrier is preferably at least about 50%, most preferably at least about 60%, by weight of the carrier. Mixtures of water and low molecular weight, e.g., <about 200, organic solvent, e.g., lower alcohols such as ethanol, propanol, isopropanol or butanol are useful as the carrier liquid. Low molecular weight alcohols include monohydric, dihydric (glycol, etc.) trihydric (glycerol, etc.), and higher polyhydric (polyols) alcohols.

(2) Dispersibility Aids

[0062] Relatively concentrated compositions containing both saturated and unsaturated diester quaternary ammonium compounds can be prepared that are stable without the addition of concentration aids. However, the compositions of the present invention may require organic and/or inorganic concentration aids to go to even higher concentrations and/or to meet higher stability standards depending on the other ingredients. These concentration aids which typically can be viscosity modifiers may be needed, or preferred, for ensuring stability under extreme conditions when particular softener active levels are used. The surfactant concentration aids are typically selected from the group consisting of (1) single long chain alkyl cationic surfactants; (2) nonionic surfactants; (3) amine oxides; (4) fatty acids; and (5) mixtures thereof. These aids are described in WO 94/20597, specifically on page 14, line 12 to page 20, line 12, which is herein

incorporated by reference.

When said dispersibility aids are present, the total level is from 0.1% to 20%, preferably from 0.2% to 10%, more preferably from 0.5% to 5%, and even more preferably from 1% to 2% by weight of the composition. These materials can either be added as part of the active softener raw material, (I), e.g., the mono-long chain alkyl cationic surfactant and/or the fatty acid which are reactants used to form the biodegradable fabric softener active as discussed hereinbefore, or added as a separate component. The total level of dispersibility aid includes any amount that may be present as part of component (I).

[0063] Inorganic viscosity/dispersibility control agents which can also act like or augment the effect of the surfactant concentration aids, include water-soluble, ionizable salts which can also optionally be incorporated into the compositions of the present invention. A wide variety of ionizable salts can be used. Examples of suitable salts are the halides of the Group IA and IIA metals of the Periodic Table of the Elements, e.g., calcium chloride, magnesium chloride, sodium chloride, potassium bromide, and lithium chloride. The ionizable salts are particularly useful during the process of mixing the ingredients to make the compositions herein, and later to obtain the desired viscosity. The amount of ionizable salts used depends on the amount of active ingredients used in the compositions and can be adjusted according to the desires of the formulator. Typical levels of salts used to control the composition viscosity are from about 20 to about 20,000 parts per million (ppm), preferably from about 20 to about 11,000 ppm, by weight of the composition. Alkylene polyammonium salts can be incorporated into the composition to give viscosity control in addition to or in place of the water-soluble, ionizable salts above. In addition, these agents can act as scavengers, forming ion pairs with anionic detergent carried over from the main wash, in the rinse, and on the fabrics, and may improve softness performance. These agents may stabilize the viscosity over a broader range of temperature, especially at low temperatures, compared to the inorganic electrolytes. Specific examples of alkylene polyammonium salts include L-lysine monohydrochloride and 1,5-diammonium 2-methyl pentane dihydrochloride.

(3)-Stabilizers

[0064] Stabilizers can be present in the compositions of the present invention. The term "stabilizer," as used herein, includes antioxidants and reductive agents. These agents are present at a level of from 0% to about 2%, preferably from about 0.01% to about 0.2%, more preferably from about 0.035% to about 0.1% for antioxidants, and more preferably from about 0.01% to about 0.2% for reductive agents. These assure good odor stability under long term storage conditions for the compositions and compounds stored in molten form. The use of antioxidants and reductive agent stabilizers is especially critical for low scent products (low perfume).

[0065] Examples of antioxidants that can be added to the compositions of this invention include a mixture of ascorbic acid, ascorbic palmitate, propyl gallate, available from Eastman Chemical Products, Inc., under the trade names Tenox[®] PG and Tenox S-1; a mixture of BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), propyl gallate, and citric acid, available from Eastman Chemical Products, Inc., under the trade name Tenox-6; butylated hydroxytoluene, available from UOP Process Division under the trade name Sustane[®] BHT; tertiary butylhydroquinone, Eastman Chemical Products, Inc., as Tenox TBHQ; natural tocopherols, Eastman Chemical Products, Inc., as Tenox GT-1/GT-2; and butylated hydroxyanisole, Eastman Chemical Products, Inc., as BHA; long chain esters (C₈-C₂₂) of gallic acid, e.g., dodecyl gallate; Irganox[®] 1010; Irganox[®] 1035; Irganox[®] B 1171; Irganox[®] 1425; Irganox[®] 3114; Irganox[®] 3125; and mixtures thereof; preferably Irganox[®] 3125, Irganox[®] 1425, Irganox[®] 3114, and mixtures thereof; more preferably Irganox[®] 3125 alone. The chemical names and CAS numbers for some of the above stabilizers are listed in Table II below.

TABLE II

Antioxidant	CAS No.	Chemical Name used in Code of Federal Regulations
Irganox [®] 1010	6883-19-8	Tetrakis (methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)) methane
Irganox [®] 1035	41484-35-9	Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)
Irganox [®] 1098	23128-74-7	N,N'-Hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide)
Irganox [®] B 1171	31570-04-4	
	23128-74-7	1:1 Blend of Irganox [®] 1098 and Irgafos [®] 168
Irganox [®] 1425	65140-91-2	Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate)
Irganox [®] 3114	65140-91-2	Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate)

TABLE II (continued)

Antioxidant	CAS No.	Chemical Name used in Code of Federal Regulations
Irganox® 3125 acid	34137-09-2	3,5-Di-tert-butyl-4-hydroxy-hydrocinnamic triester with 1,3,5-tris(2-hydroxyethyl)-S-triazine-2,4,6-(1H, 3H, 5H)-trione
Irgafos® 168	31570-04-4	Tris(2,4-di-tert-butyl-phenyl)phosphite

[0066] Examples of reductive agents include sodium borohydride, hypophosphorous acid, Irgafos® 168, and mixtures thereof.

4-Antimicrobial active

[0067] The composition may suitably use an optional solubilized, water-soluble antimicrobial active, useful in providing protection against organisms that become attached to the treated material. The free, uncomplexed antimicrobial, e.g., antibacterial, active provides an optimum antibacterial performance.

[0068] Sanitization of fabrics can be achieved by the compositions of the present invention containing, antimicrobial materials, e.g., antibacterial halogenated compounds, quaternary compounds, and phenolic compounds.

[0069] **Biguanides.** Some of the more robust antimicrobial halogenated compounds which can function as disinfectants/sanitizers as well as finish product preservatives (vide infra), and are useful in the compositions of the present invention include 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with hydrochloric, acetic and gluconic acids. The digluconate salt is highly water-soluble, about 70% in water, and the diacetate salt has a solubility of about 1.8% in water. When chlorhexidine is used as a sanitizer in the present invention it is typically present at a level of from about 0.001% to about 0.4%, preferably from about 0.002% to about 0.3%, and more preferably from about 0.01% to about 0.1%, by weight of the usage composition. In some cases, a level of from about 1% to about 2% may be needed for virucidal activity.

[0070] Other useful biguanide compounds include Cosmocil® CQ®, Vantocil® IB, including poly (hexamethylene biguanide) hydrochloride. Other useful cationic antimicrobial agents include the bis-biguanide alkanes. Usable water soluble salts of the above are chlorides, bromides, sulfates, alkyl sulfonates such as methyl sulfonate and ethyl sulfonate, phenylsulfonates such as p-methylphenyl sulfonates, nitrates, acetates, gluconates, and the like.

[0071] As stated hereinbefore, the bis biguanide of choice is chlorhexidine and its salts, e.g., digluconate, dihydrochloride, diacetate, and mixtures thereof.

[0072] **Quaternary Compounds.** A wide range of quaternary compounds can also be used as antimicrobial actives, in conjunction with the preferred surfactants, for compositions of the present invention that do not contain cyclodextrin. Non-limiting examples of useful quaternary compounds include: (1) benzalkonium chlorides and/or substituted benzalkonium chlorides such as commercially available Barquat® (available from Lonza), Maquat® (available from Mason), Variquat® (available from Witco/Sherex), and Hyamine® (available from Lonza); (2) dialkyl quaternary such as Bardac® products of Lonza, (3) N-(3-chloroallyl) hexammonium chlorides such as Dowdicol® and Dowidol® available from Dow; (4) benzethonium chloride such as Hyamine® 1622 from Rohm & Haas; (5) methylbenzethonium chloride represented by Hyamine® 10X supplied by Rohm & Haas, (6) cetylpyridinium chloride such as Cepacol chloride available from of Merrell Labs. Typical concentrations for biocidal effectiveness of these quaternary compounds range from about 0.001% to about 0.8%, preferably from about 0.005% to about 0.3%, more preferably from about 0.01% to 0.2%, by weight of the usage composition. The corresponding concentrations for the concentrated compositions are from about 0.003% to about 2%, preferably from about 0.005% to about 1.2%, and more preferably from about 0.1% to about 0.8% by weight of the concentrated compositions.

[0073] Other preservatives which are conventional in the art, such as described in US 5,593, 670 incorporated herein by reference, may also be used herein.

5-Perfume

[0074] The present invention can contain a perfume. Suitable perfumes are disclosed in U.S. Pat. 5,500,138, said patent being incorporated herein by reference.

[0075] As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such as fixatives, extenders, stabilizers and solvents. These auxiliaries are also included within the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds.

[0076] Examples of perfume ingredients useful in the perfumes of the present invention compositions include, but are not limited to, hexyl cinnamic aldehyde; amyl cinnamic aldehyde; amyl salicylate; hexyl salicylate; terpineol; 3,7-dimethyl-*cis*-2,6-octadiene-1-ol; 2,6-dimethyl-2-octanol; 2,6-dimethyl-7-octen-2-ol; 3,7-dimethyl-3-octanol; 3,7-dimethyl-*trans*-2,6-octadiene-1-ol; 3,7-dimethyl-6-octen-1-ol; 3,7-dimethyl-1-octanol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; tricyclodecanyl propionate; tricyclodecanyl acetate; anisaldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; ethyl-3-methyl-3-phenyl glycidate; 4-(para-hydroxyphenyl)-butan-2-one; 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; para-methoxyacetophenone; para-methoxy-alpha-phenylpropene; methyl-2-n-hexyl-3-oxo-cyclopentane carboxylate; undecalactone gamma.

[0077] Additional examples of fragrance materials include, but are not limited to, orange oil; lemon oil; grapefruit oil; bergamot oil; clove oil; dodecalactone gamma; methyl-2-(2-pentyl-3-oxo-cyclopentyl) acetate; beta-naphthol methyl ether; methyl-beta-naphthylketone; coumarin; decylaldehyde; benzaldehyde; 4-tert-butylcyclohexyl acetate; alpha,alpha-dimethylphenethyl acetate; methylphenylcarbinyl acetate; Schiff's base of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate; cyclic ethyleneglycol diester of tridecanedioic acid; 3,7-dimethyl-2,6-octadiene-1-nitrile; ionone gamma methyl; ionone alpha; ionone beta; petitgrain; methyl cedrylone; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene; ionone methyl; methyl-1,6,10-trimethyl-2,5,8-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; benzophenone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal; 7-hydroxy-3,7-dimethyl octanal; 10-undecan-1-ol; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecan; cyclopentadecanone; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,5,7,8-hexahydro-4,6,7,8,8-hexamethylcyclopentane-gamma-2-benzopyrane; ambroxane; dodecylhydro-3a,6,6,9a-tetramethylnaphtho-[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; cedryl acetate; para-tert-butylcyclohexyl acetate; patchouli; oilanum resinoid labdanum; vetiver; copaiba balsam; fir balsam; and condensation products of: hydroxycitronellal and methyl anthranilate; hydroxycitronellal and indol; phenyl acetaldehyde and indol; 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate.

More examples of perfume components are geraniol; geranyl acetate; linalool; linalyl acetate; tetrahydrolinalool; citronellol; citronellol acetate; dihydromyrcenol; dihydromyrcenyl acetate; tetrahydromyrcenol; terpinyl acetate; nopol; nopyl acetate; 2-phenylethanol; 2-phenylethyl acetate; benzyl alcohol; benzyl acetate; benzyl salicylate; benzyl benzoate; styrallyl acetate; dimethylbenzylcarbinol; trichloromethylphenylcarbinyl acetate; methylphenylcarbinyl acetate; isononyl acetate; vetiveryl acetate; vetiverol; 2-methyl-3-(p-tert-butylphenyl)-propanal; 2-methyl-3-(p-isobutylphenyl)-propanal; 3-(p-tert-butylphenyl)-propanal; 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde; 4-acetoxy-3-phenyltetrahydro-pyran; methyl dihydroxymonate; 2-n-heptylcyclopentanone; 3-methyl-2-pentyl-cyclopentanone; n-decanal; n-dodecanal; 9-decenol-1; phenoxyethyl isobutyrate; phenylacetaldehyde dimethylacetate; phenylacetaldehyde diethylacetate; geranonitrile; citronellonitrile; cedryl acetal; 3-isocampylcyclohexanol; cedryl methyl ether; isologifolone; aubepine nitrile; aubepine; heliotropine; eugenol; vanillin; diphenyl oxide; hydroxycitronellal isonones; methyl isonones; isomethyl isonones; irones; cis-3-hexenol and esters thereof; indane musk fragrances; tetralin musk fragrances; isochroman musk fragrances; macrocyclic ketones; macrolactone musk fragrances; ethylene brassylate.

[0078] The perfumes useful in the present invention compositions are substantially free of halogenated materials and nitromusks.

[0079] Suitable solvents, diluents or carriers for perfumes ingredients mentioned above are for examples, ethanol, isopropanol, diethylene glycol, monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, etc. The amount of such solvents, diluents or carriers incorporated in the perfumes is preferably kept to the minimum needed to provide a homogeneous perfume solution.

[0080] Perfume can be present at a level of from 0% to 10%, preferably from 0.1% to 5%, and more preferably from 0.2% to 3%, by weight of the finished composition. Fabric softener compositions of the present invention provide improved fabric perfume deposition.

[0081] Perfume ingredients may also be suitably added as releasable fragrances, for example, as pro-perfumes or pro-fragrances as described in U.S. 5,652,205 Hartman et al., issued July 29, 1997, WO95/04809, WO95/02625, PCT US97/14610 filed 19 August 1997 and claiming priority of 19 August 1996, and EP-A-0,752,465, incorporated herein by reference.

6- Soil Release Agent

[0082] Soil Release agents are desirably used in compositions of the instant invention. Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later

washing procedures.

[0083] If utilized, soil release agents will generally comprise from about 0.01 % to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

[0084] The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 3,959,230 Hays, issued May 25, 1978; U.S. 3,893,929 Basadur, issued July 8, 1975; U.S. 4,000,093, Nicol, *et al.*, issued December 28, 1976; U.S. Patent 4,702,857 Gosselink, issued October 27, 1987; U.S. 4,968,451, Scheibel *et al.*, issued November 6, U.S. 4,702,857, Gosselink, issued October 27, 1987; U.S. 4,711,730, Gosselink *et al.*, issued December 8, 1987; U.S. 4,721,580, Gosselink, issued January 26, 1988; U.S. 4,877,896, Maldonado *et al.*, issued October 31, 1989; U.S. 4,956,447, Gosselink *et al.*, issued September 11, 1990; U.S. 5,415,807 Gosselink *et al.*, issued May 16, 1995; European Patent Application 0 219 048, published April 22, 1987 by Kud, *et al.*.

[0085] Further suitable soil release agents are described in U.S. 4,201,824, Violland *et al.*; U.S. 4,240,918 Lagasse *et al.*; U.S. 4,525,524 Tung *et al.*; U.S. 4,579,681, Ruppert *et al.*; U.S. 4,240,918; U.S. 4,787,989; U.S. 4,525,524; EP 279,134 A, 1988, to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N. V., 1974 all incorporated herein by reference.

[0086] Commercially available soil release agents include the METOLOSE SM100, METOLOSE SM200 manufactured by Shin-etsu Kagaku Kogyo K.K., SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (Germany), ZELCON 5126 (from Dupont) and MILEASE T (from ICI).

7-pH

[0087] An optional requirement of the compositions according to the present invention is that the pH is greater than 3, preferably between 3 and 12. This range is preferred for fabric safety. When a lubricant of the diester quaternary ammonium type is used, it is most preferred to have the conventional pH range, as measured in the neat compositions at 20 °C, of from 2.0 to 5, preferably in the range of 2.5 to 4.5, preferably about 2.5 to about 3.5. The pH of these compositions herein can be regulated by the addition of a Bronsted acid.

9- Other Optional Ingredients

[0088] The present invention can include optional components conventionally used in textile treatment compositions, for example, colorants, preservatives, bactericides, optical brighteners, opacifiers, anti-shrinkage agents, germicides, fungicides, anti-oxidants, dye fixing agent, enzymes, chelating agents, cyclodextrin, metallic salts to absorb amine and sulfur-containing compounds and selected from the group consisting of copper salts, zinc salts, and mixtures thereof, color protectors like polyethylene mine and its alkoxylated derivatives, and the like. The compositions are preferably free of any material that would soil or stain fabric, and are also substantially free of starch. Typically, there should be less than about 0.5%, by weight of the composition, preferably less than about 0.3%, more preferably less than about 0.1 %, by weight of the composition, of starch and/or modified starch.

Form of the composition and compounds

[0089] The composition or its individual components can be provided in any suitable form such as spray, foam, gel or any other suitable form for liquid aqueous compositions.

Method of use

[0090] There is provided a method of treating fabrics, in particular to provide durable press on fabric, i.e. for providing wrinkle resistant fabrics, which comprises the steps of contacting the fabrics with a cross-linking compound or composition of the invention, as defined herein before, and subsequently curing the composition using a domestic process.

[0091] By "contacting", it is meant any steps that is suitable for providing a contact of the composition with the fabric. This can include by soaking, washing, rinsing, and/or spraying as well as by means of a dryer sheet onto which is adsorbed the composition. Preferably, the contacting occurs in the step of a laundering process, preferably a rinse step of a laundry process, which more preferably occurs at a temperature range below 30°C, preferably between 5 and 25°C.

[0092] Domestic curing of the fabric can be caused by the heat used to dry the fabric, e.g. by tumble drying. Ironing is also particularly advantageous for curing the fabric. Without to be bound by theory, it is believed that the shorter time or the low temperatures used to domestically cure the cross-linking components mean that the fabric is made resistant to wrinkles without changing its tactile, or drape properties.

[0093] Still another advantage of the present invention is that when epichlorhydrin adducts of polyamine resins, polyethyleneimine resins, cationic starch, or polydiallyldimethylammonium chloride are used, such as in particular with Kymene compounds, the domestic curing can occur at room temperature, i.e. from 15 to 30°C.

[0094] Still a further advantage of the above mentioned epichlorohydrin adducts is their usability in industrial treatment. Accordingly, there is also provided a method for treating fabric which comprises the steps of contacting the fabrics with an epichlorohydrin adduct of polyamine resins, polyethyleneimine resins, cationic starch, or polydiallyldimethylammonium chloride, or mixtures thereof, and thereafter curing the fabrics. In this preferred method, the curing is that which is conventionally known in industrial process like padding.

[0095] The composition of the present invention can also be used as an ironing aid. An effective amount of the composition can be sprayed onto fabric, wherein said fabric should not be sprayed to saturation. The fabric can be ironed at the normal temperature at which it should be ironed. Still another preferred way of treating the fabrics is when the fabric can be sprayed with an effective amount of the composition, allowed to dry and then ironed, or sprayed and ironed immediately.

[0096] The invention is illustrated in the following non limiting examples, in which all percentages are on a weight basis unless otherwise stated.

[0097] In the examples, the abbreviated component identifications have the following meanings:

Resin #1	Polyamide/polyamine/epichlorohydrin resin commercially available under the tradename KYMENE 557 from Hercules Inc.
Resin #2	Polyamide/polyamine/epichlorohydrin resin commercially available under the tradename KYMENE 450 from Hercules Inc.
Resin #3	Melamine-formaldehyde resin commercially available under the tradename CASSURIT HML from Clariant
Resin #4	Poly(acrylamide-glyoxal) resin commercially available under the tradename SOLIDURIT KM from Clariant
Resin #5	Melamine-formaldehyde resin commercially available under the tradename MADURIT MW 167 from Clariant
Catalyst	: Catalyst NKD, made of a mixture of salts and organic acid, and commercially available from Hoechst
DEQA	: Di-(tallowyl-oxy-ethyl) dimethyl ammonium chloride
DOEQA	: Di-(oleoxyethyl) dimethyl ammonium methylsulfate
DTDMAC	: Ditalow dimethylammonium chloride
Fatty acid	: tallow fatty acid IV=18
Electrolyte	: Calcium chloride
PEG	: Polyethylene Glycol 4000
PEI 1800 E1	: Ethoxylated polyethylene imine (MW 1800, at 50% active) as synthesised in Synthesis example 1
PEI 1200 E7	: Ethoxylated polyethylene imine (MW 1200, at 50% active in water) as synthesised per Synthesis example 2
Dye Fix 1	: Cellulose reactive dye fixing agent available under the tradename Indosol CR from Clariant

Synthesis Example 1-Preparation of PEI 1800 E1

[0098]

Step A)-The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (Nippon Shokubai, Epomin SP-018 having a listed average molecular weight of 1800 equating to 0.417 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Step B)- The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C. The final reaction product is cooled slightly and collected in glass containers purged with nitrogen. In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

Synthesis Example 2-Preparation of PEI 1200 E₁

[0099]

Step A)-The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A -20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (having a listed average molecular weight of 1200 equating to about 0.625 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Step B)- The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130°C. The final reaction product is cooled slightly and collected in glass containers purged with nitrogen. In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

[0100] If a PEI 1200 E₇ is desired, the following step of catalyst addition will be included between Step A and B.

Vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130°C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110° C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methane sulfonic acid (1.74 moles).

[0101] Other preferred examples such as PEI 1200 E₂, PEI 1200 E₃, PEI 1200 E₁₅ and PEI 1200 E₂₀ can be prepared by the above method by adjusting the reaction time and the relative amount of ethylene oxide used in the reaction.

[0102] The invention is illustrated in the following non limiting examples, in which all percentages are on a weight basis unless otherwise stated.

Example

[0103] The following compositions A to J are in accordance with the invention.

	A	B	C	D	E	F	G	H	I	J
Resin#1	15	-	-	-	-	-	-	-	-	12
Resin#2	-	25	-	-	-	-	-	-	15	-
Resin#3	-	-	50	50	50	10	-	-	-	-
Resin#4	-	-	-	-	-	-	30	-	-	-
Resin#5	-	-	-	-	-	-	-	30	30	30
DEQA	-	-	5	-	5	1	-	5	5	5
DOEQA	-	5	-	-	-	-	5	-	-	-
DTDMAC	10	-	-	-	-	-	-	-	-	-
Fatty acid	-	-	-	-	-	2	-	-	-	-
Electrolyte	-	-	-	-	-	-	-	-	-	2
PEG	-	-	-	3	-	-	-	-	2	-
PEI 1800 E1	-	-	-	-	-	-	-	10	-	-
PEI 1200 E7	-	-	-	-	5	-	-	-	5	-
Dye Fix 1	-	-	-	-	5	-	-	-	5	3
Catalyst	-	-	20	-	20	3	10	10	-	-
water and minors to balance to 100%										

Claims

1. A composition comprising:

- i)-a fabric softening compound; and
- ii)-a cross-linking resin having the property of being cationic.

2. A composition according to Claim 1, wherein said cross-linking resin compound is selected from amine-aldehyde resins, amide-aldehyde resins, epichlorohydrin adducts of polyamines, polyethyleneimines, cationic starches, polydiallyldimethylammonium chloride, and mixtures thereof, and mixtures thereof.

3. A composition according to Claim 1, wherein said cross-linking resin is a polyamine epichlorohydrin resin selected from selected from the group consisting of a polyamide-epichlorohydrin, a polyalkylenepolyamine-epichlorohydrin, and an amine polymer-epichlorohydrin.

4. A composition according to any one of Claims 1-3, wherein said cross-linking resin has a molecular weight between 200 and 1,000,000, preferably between 500 and 100,000.

5. A composition according to any one of Claims 1-4, wherein said cross-linking resin is present in an amount of from 0.01 % to 60%, preferably from 0.01% to 30% by weight of the total composition.

6. A composition according to any one of Claims 1-5, wherein said cross-linking resin is an aldehyde containing cross-linking resin, and wherein said composition further comprises a catalyst, preferably present in an amount of from 10% to 50%, by weight of the cross-linking components or derivative thereof.

7. A composition according to any one of Claims 1-6, wherein the softening compound is a quaternary ammonium

compounds or amine precursors thereof

8. A method of treating fabrics which comprises the steps of

- 5 i)-contacting the fabrics with a resin compound or composition as defined in any one of Claims 1-7, and
 ii)- curing the composition using a domestic process.

9. A method of treating fabrics which comprises the steps of:

- 10 i)-contacting the fabrics with an epichlorohydrin adducts of polyamines, polyethyleneamines, cationic starches,
 polydiallyldimethylammonium chloride, and mixtures thereof and
 ii)- curing the composition.

10. A method according to either one of Claim 8 or 9, wherein said contacting occurs in the rinse process.

11. A method according to any one of Claims 8-10, wherein said contacting occurs at a temperature range below 30°C,
preferably between 5 and 25°C.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 87 0173

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	WO 91 19037 A (PROCTER & GAMBLE) 12 December 1991 * claims *	1,8	C11D3/00 C11D3/37 C11D3/22 D06M15/423
A	WO 96 15310 A (PROCTER & GAMBLE) 23 May 1996 * page 14, line 11 - page 16, line 14 *	1,8	D06M15/11 D06M15/61 D06M13/463
A	US 4 376 633 A (REINHARDT ROBERT M ET AL) 15 March 1983 * column 3, line 23 - line 44 *	1,8	
A	EP 0 363 346 A (PROCTER & GAMBLE) 11 April 1990 * page 3, line 40 - page 5, line 31 * * page 7; claims *	1,8	
A	GB 861 693 A (SHRI RAM INSTITUTE FOR INDUSTRIAL RESEARCH) 22 February 1961 * example 1 *	1,8	
A	US 2 974 432 A (WARNOCK, WILLIAM K. ET AL.) 14 March 1961 * column 2, line 37 - column 3, line 7 *	1,8	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D D06M
A	DATABASE WPI Section Ch, Week 9838 Derwent Publications Ltd., London, GB; Class A14, AN 98-440579 XP002089807 * JP 10 183472 A (KAO CORP), 14 July 1998 * abstract *	1,8	
A,D	WO 98 04772 A (MOONEY WILLIAM ; UNILEVER PLC (GB); UNILEVER NV (NL)) 5 February 1998 * claims 1,2 *	1,8	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 January 1999	Examiner Herrmann, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document	

EPIC FORM 1000 (3.9.98) (P/N 4001)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 87 0173

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-01-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9119037 A	12-12-1991	US 5064543 A	12-11-1991
		US 5062971 A	05-11-1991
		US 5336419 A	09-08-1994
		AU 8057691 A	31-12-1991
		CN 1059001 A	26-02-1992
		EP 0532671 A	24-03-1994
WO 9615310 A	23-05-1996	BR 9509716 A	21-10-1997
		EP 0791096 A	27-08-1997
		JP 10508912 T	02-09-1998
		US 5798107 A	25-08-1998
		ZA 9509558 A	05-06-1996
US 4376633 A	15-03-1983	NONE	
EP 0363346 A	11-04-1990	US 4911852 A	27-03-1990
		AU 638941 B	15-07-1993
		AU 4263689 A	12-04-1990
		CA 2000195 A,C	07-04-1990
		CN 1041971 A	09-05-1990
		JP 2169697 A	29-06-1990
		MX 165879 B	08-12-1992
		PH 25989 A	13-01-1992
GB 861693 A		NONE	
US 2974432 A	14-03-1961	GB 862653 A	
WO 9804772 A	05-02-1998	AU 3622997 A	20-02-1998

EPO FORM P4009

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 096 056 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
02.05.2001 Bulletin 2001/18

(51) Int Cl.7: **D06M 15/11, D06M 15/423,
D06M 15/61, C08L 39/06**

(21) Application number: **99870222.9**

(22) Date of filing: **27.10.1999**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
Cincinnati, Ohio 45202 (US)

(72) Inventors:
• **Altmann, Markus W.**
1050 Brussels (BE)

• **Hubesch, Bruno Albert Jean**
3040 Neerijse-Huldenberg (BE)
• **Soyez, Hedi Simonne Marlette**
8400 Oostende (BE)

(74) Representative: **Gault, Nathalie et al**
BVBA Procter & Gamble Europe Sprl
Temseleaan 100
1853 Strombeek-Bever (BE)

(54) Wrinkle resistant composition

(57) There is provided a wrinkle reducing composition comprising a cross-linking resin having the property of being cationic and a component having the property of being co-cross linked with the resin and/or a component comprising at least one unit which provides a dye transfer inhibiting benefit; and article of manufacture thereof. Also herein provided are method of treating fabrics

rics for imparting various benefits including reducing wrinkles; improving the natural drape of fabrics, imparting a crisp finish to fabrics, reducing the time and/or effort involved to iron fabrics, imparting crease resistance to fabrics, imparting post wash wrinkle resistance to fabrics, imparting in-wear wrinkle resistance to fabrics, imparting a reduction of the fabric aging upon multiple application.

EP 1 096 056 A1

Description

Technical field of the invention

- 5 [0001] The present invention relates to fabric care compositions and to a method for treating fabrics in order to improve various properties of fabrics, in particular, wrinkle resistance.

Background of the invention

- 10 [0002] Wrinkles in textile fabrics are caused by the bending and creasing of the textile material which places an external portion of a filament in a yarn under tension while the internal portion of that filament in the yarn is placed under compression. Particularly with cotton fabrics, the hydrogen bonding that occurs between the cellulose molecules contributes to keeping wrinkles in place. The wrinkling of fabric, in particular clothing, is therefore subject to the inherent

- 15 [0003] In the modern world, with the increase of hustle and bustle and travel, there is a demand for a quick fix which will help to diminish the labor involved in home laundering and/or the cost and time involved in dry cleaning or commercial laundering. Further, it is well known that alternating cycles of using and laundering fabrics and textiles, such as articles of worn clothing and apparel, will inevitably adversely affect the appearance and integrity of the fabric and textile items so used and laundered. Fabrics and textiles simply wear out over time and with use. Laundering of fabrics and textiles is necessary to remove soils and stains which accumulate therein and thereon during ordinary use. However, the laundering operation itself, over many cycles, can accentuate and contribute to the deterioration of the integrity and the appearance of such fabrics and textiles. Accordingly, this has brought additional pressure to bear on textile technologists to produce a product that will sufficiently reduce wrinkles in fabrics, especially clothing, and to produce a good appearance through a simple, convenient application of a product.

- 25 [0004] The prior art contains numerous examples of compositions for reducing wrinkles. U.S. 5,532,023, discloses aqueous wrinkle control compositions containing non-volatile silicone and film forming polymer. Preferred silicones include reactive silicones and amino-functional silicone, known as "aminodimethicone". The composition containing such silicones is applied to fabric from a spray dispenser. It is found that in the spray treatment, an appreciable amount of the aqueous composition misses the fabric, and instead falls on flooring surfaces, such as rugs, carpets, concrete floors, tiled floors, linoleum floors, bathtub floors, which leaves a silicone layer that is accumulated on and/or cured on and/or bonded to the flooring surfaces. Such silicones that are accumulated on such surfaces, and especially those that are bonded to such surfaces are difficult to remove. Flooring surfaces thus become slippery and can present a safety hazard to the household members. U.S. 5,573,695 discloses an aqueous wrinkle removal composition containing a vegetable oil based cationic quaternary ammonium surfactant, and an anionic fluorosurfactant. Similarly, U.S. 35 4,661,268 discloses a wrinkle removal spray comprising an aqueous alcoholic composition containing a dialkyl quaternary ammonium salt and a silicone surfactant and/or a fluoro surfactant. U.S. 5,100,566 discloses a method of reducing wrinkles in fabric by spraying the fabric with an aqueous alcoholic solution of an anionic silicate alkali metal salt. U.S. 4,806,254 discloses fabric wrinkle removal aqueous alcoholic solution containing glycerine and a nonionic surfactant. W098/04772 provides the treatment of fabric against fabric creasing by application of a composition comprising a polycarboxylic acid or derivative thereof; and then curling the composition using a domestic process. These patents are incorporated herein by reference.

- 40 [0005] Accordingly, the domestic treatment of fabric is a problem known in the art to the formulator of laundry compositions.

- [0006] In addition, the problem of wrinkle reduction in industrial field is known in the art. Hence, processes for the industrial durable press treatment of textile fabrics were first introduced in the 1960's and have achieved widespread use since that time. These durable press treatment processes typically involve treating the fibers of the textile fabrics with cross-linking agents. Early durable press processes used formaldehyde as a cross-linking agent which, although effective, was highly odorous and undesirable to the consumer.

- 50 [0007] As a consequence, formaldehyde was replaced by reactive resins such as dimethylol urea (DMU), dimethylol ethylene urea (DMEU), and by modified ethylene urea resins, such as dimethylol dihydroxy ethylene urea (DMDHEU). However, still it is known that the desired increases in the durable press performance through the use of cross-linking agents are sometimes accompanied by undesirable losses in other important fabric properties, such as tensile strength, tear strength, abrasion resistance and fabric hand.

- 65 [0008] Further, solutions obtained from industry are not usually transposable to domestic treatments. Indeed, in industrial processes a strict control over parameters such as pH, electrolyte concentration, water hardness, temperature, etc., is possible whereas in a domestic washing machine, such a high level of control is not possible. One typical example is given in G3-2,185,499, which provides the use of a polyamide-epichlorohydrin resin in a dip-pad industrial process wherein the polymer is used in the presence of an acrylic polymer. However, such a composition would not

be suitable for conventional domestic process involving a curing step, like ironing. Indeed, it has been found that acrylic polymer in presence of the polyamide-epichlorhydrin resin forms precipitates, thereby leaving undesirable residues on the treated fabrics.

[0009] In addition, domestic durable press treatments require conditions that industrial treatments do not have to fulfill. Hence, for domestic durable treatments, the compounds or compositions thereof need to manifest at least one of the following properties:

i)-provide a low level of aldehyde; indeed aldehyde based cross-linker technologies are less favoured in domestic process from an environmental and safety standpoint because contrary to industry where the process is controlled, in domestic process the consumer is the only person using the product, thus enabling the possibility of misuse. Further, high levels of aldehyde tends to produce an odour which would deter the consumer from using it again. Thus, it is desired to provide durable processes for use in domestic process which are safe to the consumer and provide a good odour acceptance;

ii)-provide a low or even no tensile strength loss; again as stated above for i), the control of the process in domestic treatment is less measurable. Further, contrary to industry where the fabrics are treated once, domestic treatment involves repeated usage and thus produce a tensile strength loss. Thus, it is desired to provide durable processes for use in domestic process which provide a low or even no tensile strength loss;

iii)-be usable at low temperature; indeed in a domestic process, and in particular in a domestic rinse process, it is not practical to rely on high treatment temperatures such as those used in industrial processes. Thus, it is also a further desire of domestic durable press to provide a better performance at low temperatures. Indeed, industry usually achieves a better performance by close control of the reaction process and its various parameters involved; whereas in domestic treatment this close control cannot be achieved. Consequently, the performance of the durable press process needs mostly to be achieved by use of efficient technology, instead of process features;

iv)-be applicable in rinse applications as well as in other domestic treatment like laundry machine, soaking, pre-treatment; in such type of application, easier control of the use of the product is achieved, thereby avoiding misuse. Thus, for domestic treatment, the technology involved in the durable press process needs preferably to be suitable for use in one of such application.
and/or

v)-not provide stiffness to fabrics. Again, as described for ii), the repeated usage that are involved in domestic treatment may also lead to stiff fabric. Accordingly, it is desired to provide durable press process which reduces such negative.

[0010] In addition to the above, industrial processes use high concentrations of cross-linking agents which is required for industrial scale treatment whilst for domestic treatment a low level is still preferred for economical reasons.

[0011] Accordingly, notwithstanding the advances in the art, there is still a need for an efficient and economical composition which provides effective domestic durable press properties on the treated fabrics.

[0012] Recently, a new class of materials, namely the polyamide-epichlorhydrin resins, conventionally known in the paper industry under the tradename Kymene, have found increasing use in the domestic treatment of fabrics in order to provide durable press benefits. One typical disclosure is given in co-pending European patent application No. 98670173. That application also exemplifies a combination of 15% polyamide/polyamine/epichlorhydrin polymers (Kymene polymers) with 5% polyethylene imine with 7 ethoxylations. In addition, polyamide-epichlorhydrin resins are known for use in industrial treatment, but with the disadvantages highlighted above.

[0013] It has now surprisingly been found that a cross-linking resin having the property of being cationic, in particular polyamide-epichlorhydrin resins, are stabilized in the presence of a component having the property of being co-cross linkable with the resin and/or a component, preferably polymer, comprising at least one unit which provides a dye transfer inhibiting benefit. Not to be bound by any theory, it is believed that by the addition of such polymer, electrostatic interactions between the cationic group of the resin and the polar group of the polymer occur thereby resulting in a so-called "polyelectrolyte complex". As a result, a synergistic benefit on crease resistance as well as on fabric appearance like better dewrinkling, better colour protection, and/or reduced abrasion is observed.

[0014] Still surprising, it has also been found that the use of this combination shows a synergistic increase performance as to the crease resistance and fabric crispness/hand on the treated fabrics. Further, by use of this compositions, conditions i) to v) are still fulfilled.

[0015] Accordingly, the present invention reduces wrinkles in fabrics, including clothing, dry cleanables, linens, bed clothes, and draperies, by ironing. The present invention can be used on damp or dry clothing to relax wrinkles and

give clothes a ready to wear or use look that is demanded by today's fast paced world.

[0016] In a preferred aspect, an additional benefit of the composition of the present invention is an improved garment shape, body and crispness.

[0017] The composition of the present invention acts as an excellent ironing aid. The present invention makes the task of ironing easier and faster by creating less iron drag. The compositions of the present invention help produce a crisp, smooth appearance.

Summary of the invention

[0018] The present invention is a wrinkle reducing composition comprising:

- a)-a cross-linking resin having the property of being cationic; and
- b)-a component having the property of being co-cross linkable with the resin and/or a component comprising at least one unit which provides a dye transfer inhibiting benefit;

with the proviso that when the cross-linking resin is a polyquaternary amine resin of the polyamide/polyamine/epichlorohydrin type present in amount of 15% by weight, the amino functional polymer is not a polyethylene imine with 7 ethoxylations present in amount of 5% by weight.

[0019] In another aspect of the invention, there is provided an article of manufacture comprising the composition of the invention.

[0020] Still in a further aspect of the invention, there is provided a method of treating fabrics for imparting benefits selected from the group consisting of: reducing wrinkles; improving the natural drape of fabrics, imparting a crisp finish to fabrics, reducing the time and/or effort involved to iron fabrics, imparting crease resistance to fabrics, i.e. imparting post wash wrinkle resistance to fabrics as well as imparting in-wear wrinkle resistance to fabrics, imparting a reduction of the fabric aging upon multiple application. By "post wash wrinkle resistance" it is meant, wrinkle resistance during several laundry cycles; by "in-wear wrinkle resistance" it is meant, wrinkle resistance during wear of the garments and by "fabric aging" it is meant color loss, abrasion, pilling or fuzzing of the fabric.

[0021] In a further aspect of the invention, there is provided an article of manufacture comprising a container and the composition of the invention in association with instructions to use.

Detailed description of the invention

1)-Cross-linking resin having the property of being cationic

[0022] An essential component of the invention is a cross-linking resin having the property of being cationic. By "cross-linking resin having the property of being cationic", it is meant that the resin is at least partially positively charged. It is not however necessary that the reactive part of the molecule carries the positive charge. Indeed, polymeric resins can be based on positively charged monomers which help the deposition on the fibers. Since the cross-linking resins are cationic, i.e. positively charged, they are deposited and well retained on the negatively charged cellulosic fibers when these resins are added to the final rinse of a laundry process.

[0023] Cross-linking resins having the property of being cationic suitable for use herein are those commonly known as having wet strength in the paper field. At least two mechanisms have been postulated to account for the mechanism by which wet strength resin act. One is that wet strength resins form covalent bonds between adjacent fibers while another is that the wet strength resin places a layer over the hydrogen bonds formed between adjacent paper fibers and thus prevents water from breaking the hydrogen bonds.

[0024] Conventional wet-strength agents suitable for use herein include compounds made of epichlorohydrin adducts of polyamine resins, polyethyleneimine resins, cationic starch, polydiallyldimethylammonium chloride, and mixtures thereof, amine-aldehyde resins such as melamine-formaldehyde resin, amide-aldehyde resins, and mixtures thereof.

For use within the meaning of the present invention, there can also be used materials of the above-mentioned classes of substances which admittedly do not themselves possess any outstanding wet-strength properties but, nevertheless, have the same durable press effect as do the wet-strength agents as described therein.

[0025] Among the class of epichlorohydrin adducts of polyamine resins, polyethyleneimine resins, cationic starch, polydiallyldimethylammonium chloride, and mixtures thereof, the preferred components are the polymeric amine-epichlorohydrin resins selected from the group consisting of a polyamide-epichlorohydrin (PAE) resin, a polyalkylenepolyamine-epichlorohydrin (PAPAE) resin, and an amine polymer-epichlorohydrin (APE) resin, in which the amine groups have been alkylated with epichlorohydrin to produce a polyamine-epichlorohydrin resin that has azetidinium or epoxide functionality. Preferably, for use herein, the cross-linking resin having cationic properties is a cationic wet strength resin that is produced by reacting a saturated aliphatic dicarboxylic acid containing three to ten carbon atoms with a poly-

alkylenepolyamine, containing from two to four ethylene groups, two primary amine groups, and one to three secondary amine groups (such as diethylenetriamine, triethylenetetramine and tetraethylenepentamine), to form a poly(aminoamide) having secondary amine groups that are alkylated with epichlorohydrin to form a PAE resin.

[0026] These polyamide/polyamine/epichlorohydrin wet-strength resins are fully described by Carr, Doane, Hamerstrand and Hofreiter, in an article appearing in the Journal of Applied Polymer Science Vol. 17, pp. 721-735 (1973). Such resins are available as KYMENE from Hercules, Inc. A commercial synthesis of such resins from adipic acid, diethylene triamine and epichlorohydrin is described in the Carr et al publication, *ibid.*, and is U.S. Pat. No. 2,926,154 (Feb. 23, 1960) to G. I. Keim or US 4,240,995. Reference can be made to these publications for further details regarding the preparation of polyamide/polyamine/epichlorohydrin resins.

[0027] Most preferred cross-linking resin having cationic properties from this class are the wet strength resin Kymene 557H (available from Hercules Incorporated), in which adipic acid is reacted with diethylenetriamine to form a poly (aminoamide) that is alkylated and crosslinked with epichlorohydrin to form a PAE resin. Still another preferred cross-linking resin having cationic properties made of epichlorohydrin are Luresin.RTM and Etadurin which both are polyamidoamine-epichlorohydrin resins.

[0028] Amine-aldehyde resins are suitable cross-linking resins for the present invention and are made by condensation of amine or amide monomers with aldehydes such as formaldehyde or glyoxal. Preferred amines are those having low molecular weight amines e.g. melamine or polymeric amines e.g. poly-diallylamine, preferably quarternized. Preferred amides are those polymeric amides such as polyacrylamide. All these suitable amine/amide monomers can also be copolymerized with cationic monomers.

[0029] Among the class of amine-aldehyde cross-linking resin, preferred are those from the class of melamine-formaldehyde resin. Melamine-formaldehyde resins of this type are known as crosslinking agents of this type in the coating industry and are also described, for example, in German Auslegeschrift Nos. 2,457,387 (U.S. Pat. No. 4,035,213 incorporated herein by reference) and 1,719,324 and, in particular, in U.S. Pat. No. 3,242,230 incorporated herein by reference.

[0030] Preferred melamine-formaldehyde resin are those commercially available under the tradenames Madurit, and Cassurit from Clariant.

[0031] Still other preferred cross-linking resin having the property of being cationic among the class of amine-aldehyde cross-linking resin are the Poly(acrylamide-glyoxal) resin commercially available under the tradename SOLI-DURIT KM from Clariant.

[0032] According to the present invention, there can also be used a mixture of wet-strength agents of the above-mentioned types or equivalent compounds.

[0033] Preferably for the purpose of the invention, the cross-linking resin having cationic properties have a molecular weight between 200 and 1,000,000, preferably between 500 and 100,000, most preferably between 1000 and 25,000. Cross-linking resin having a low molecular weight are most preferred for use in the present invention as they are more water-soluble and have a better fiber penetration. By low molecular weight it is meant a molecular weight within the range of from 25 to 2000, preferably from 50 to 1000, and more preferably from 50 to 500.

[0034] The above cross-linking components may be used in a composition for delivery onto fabric, such as by means of a spray process.

[0035] It is desirable if the level of cross-linking components or derivative thereof is present in an amount of from 0.01% to 60%, preferably from 0.1% to 30% by weight of the total composition. Typically, the level of cross-linking component is present in the composition in a sufficient amount to result in an amount of from 0.01% to 60%, preferably of from 0.1 to 30%, by weight of cross-linking component per weight of dry fabrics.

[0036] It is advantageous for aldehyde containing cross-linking resins if a catalyst is used with compositions of the invention. Preferred catalysts includes organic acids such as citric acid, succinic acid, and tartaric acids, as well as conventional Lewis acid such as $AlCl_3$ or $MgCl_2$, or salts thereof, or mixtures thereof. A typical example of catalyst is the catalyst NKD made of a mixture of salts and organic acid, and commercially available from Hoechst.

[0037] It is preferred if the level of catalyst is from 10% to 50%, preferably from 20 to 40% by weight of the cross-linking components or derivative thereof.

[0038] For other cross-linking resins like the Kymene, the use of a catalyst is not necessary.

2)-Component having the property of being co-cross linkable with the resin and/or a component comprising at least one unit which provides a dye transfer inhibiting benefit

[0039] A component having the property of being co-cross linkable with the resin and/or a component comprising at least one unit which provides a dye transfer inhibiting benefit are also essential components of the invention. By use of this component(s) with the resin, a synergistic increase in performance as to the crease resistance and fabric crispness/hand on the treated fabrics is obtained, in particular from duration standpoint. Indeed, the obtained benefits from a one-shot treatment have been shown to sustain over multiple wash cycles, e.g. of about 20 wash cycles. Of course,

the treatment with the invention composition can still be effected after each wash cycle, thereby further increasing the duration of the benefit treatment, even while wearing. Still, the use of that type of component having the property of being co-cross linkable with the resin or a component comprising at least one unit which provides a dye transfer inhibiting benefit has been found particularly beneficial to the stability of the resin, in particular those that are made of polyquaternary amine resins. Indeed, a clear homogenous solution is obtained.

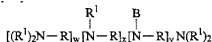
[0040] Preferred components having the property of being co-cross linkable with the resin are selected from polyamine polymers, amino-functional silicones, alkyl amines, and mixtures thereof.

[0041] The compositions of the present invention typically comprise from about 0.01 %, preferably from about 0.1 % to about 20%, preferably to about 10% by weight, of a component having the property of being co-cross linkable with the resin and/or a component comprising at least one unit which provides a dye transfer inhibiting benefit.

Polyamine polymers

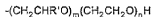
[0042] Polyamine polymers are suitable amino-functional polymers for use herein.

[0043] A preferred polyamine polymer has the formula:



wherein R, R¹ and B are suitably described in U.S. 5,565,145 Watson et al., issued October 15, 1996 incorporated herein by reference, and w, x, and y have values which provide for a backbone prior to substitution of preferably at least about 1200 daltons, more preferably 1800 daltons.

[0044] R¹ units are preferably alkyleneoxy units having the formula:



wherein R' is methyl or ethyl, m and n are preferably from about 0 to about 50, provided the average value of alkoxylation provided by m + n is at least about 0.5.

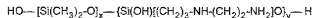
[0045] A further description of polyamine polymers suitable for use in the present invention is found in U.S. 4,891,160 Vander Meer, issued January 2, 1990; U.S. 4,597,898, Vander Meer, issued July 1, 1986; European Patent Application 111,965, Oh and Gosselink, published June 27, 1984; European Patent Application 111,984, Gosselink, published June 27, 1984; European Patent Application 112,592, Gosselink, published July 4, 1984; U.S. 4,548,744, Connor, issued October 22, 1985; and U.S. 5,565,145 Watson et al., issued October 15, 1996; all of which are included herein by reference.

[0046] Preferred polyamines are linear and branched polyethylenediamines commercially available ex BASF under the tradename Lupasol®.

Amino-functional silicones

[0047] Amino-functional silicones are also useful components having the property of being co-cross linked with the resin for use herein. Typically, these component are conventionally known under the name of silicone lubricant. Preferred aminofunctional silicones are amodimethicone compounds commercially available ex Dow Corning under the tradename DC X (where X is preferably 949 or 939).

[0048] Suitable silicone materials include materials of the formula:

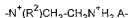
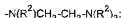


wherein x and y are integers which depend on the molecular weight of the silicone, preferably having a viscosity of from about 10,000 cst to about 500,000 cst at 25°C. This material is also known as "amodimethicone". Although silicones with a high number, e.g., greater than about 0.5 millimolar equivalent of amine groups can be used, they are not preferred because they can cause fabric yellowing.

[0049] Similarly, silicone materials which can be used correspond to the formulas:



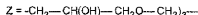
wherein G is selected from the group consisting of hydrogen, phenyl, OH, and/or C₁-C₃ alkyl; a denotes 0 or an integer from 1 to 3; b denotes 0 or 1; the sum of n + m is a number from 1 to about 2,000; R¹ is a monovalent radical of formula C_pH_{2p+1}L in which p is an integer from 2 to 8 and L is selected from the group consisting of:



wherein each R² is chosen from the group consisting of hydrogen, phenyl, benzyl, saturated hydrocarbon radical, and each A⁻ denotes compatible anion, e.g., a halide ion; and



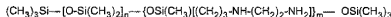
wherein



R³ denotes a long chain alkyl group; and
f denotes an integer of at least about 2.

[0050] In the formulas herein, each definition is applied individually and averages are included.

[0051] Another silicone material which can be used, but is less preferred than polydimethyl siloxanes, has the formula:



wherein n and m are the same as before. The preferred silicones of this type are those which do not cause fabric discoloration.

[0052] Alternatively, the silicone material can be provided as a moiety, or a part, of a non-silicone molecule. Examples of such materials are copolymers having siloxane macromers grafted thereto, which meet the functional limitations as defined above. That is, the non-silicone backbone of such polymers should have a molecular weight of from about 5,000 to about 1,000,000, and the polymer should have a glass transition temperature (T_g), i.e., the temperature at which the polymer changes from a brittle vitreous state to a plastic state, of greater than about -20°C.

Alkyl amines

[0053] Alkyl amines are also useful components, consisting of one or more linear or branched alkyl chains covalently linked onto a nitrogen atom. Preferred, but non-limiting examples of alkyl amines are methyl-, ethyl-, dimethyl-, diethyl-, and triethylamine.

Polymers comprising at least one unit which provide a dye transfer inhibiting benefit

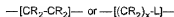
[0054] The preferred polymers comprising at least one unit which provide a dye transfer inhibiting benefit are water-soluble polymers. For the purposes of the present invention the term "water-soluble" is defined as "a polymer which when dissolved in water at a level of 0.2% by weight, or less, at 25° C, forms a clear, isotropic liquid".

[0055] The polymers comprising at least one unit which provide a dye transfer inhibiting benefit useful in the present invention have the formula:



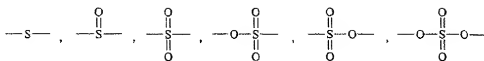
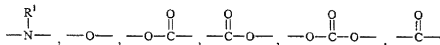
wherein the unit P is a polymer backbone which comprises units which are homopolymeric or copolymeric, D units are defined herein below. For the purposes of the present invention the term "homopolymeric" is defined as "a polymer backbone which is comprised of units having the same unit composition, i.e., formed from polymerization of the same monomer". For the purposes of the present invention the term "copolymeric" is defined as "a polymer backbone which is comprised of units having a different unit composition, i.e., formed from the polymerization of two or more monomers".

[0056] P backbones preferably comprise units having the formula:



wherein each R unit is independently hydrogen, C₁-C₁₂ alkyl, C₆-C₁₂ aryl, and D units as described herein below; preferably C₁-C₄ alkyl.

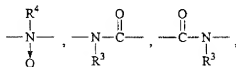
[0057] Each L unit is independently selected from heteroatom-containing moieties, non-limiting examples of which are selected from the group consisting of:



polysiloxane having the formula:



wherein the index p is from 1 to about 6; units which have dye transfer inhibition activity:

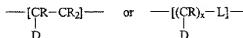


and mixtures thereof; wherein R¹ is hydrogen, C₁-C₁₂ alkyl, C₆-C₁₂ aryl, and mixtures thereof. R² is C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy, C₆-C₁₂ aryloxy, and mixtures thereof; preferably methyl and methoxy. R³ is hydrogen C₁-C₁₂ alkyl, C₆-C₁₂ aryl, and mixtures thereof; preferably hydrogen or C₁-C₄ alkyl, more preferably hydrogen. R⁴ is C₁-C₁₂ alkyl, C₆-C₁₂ aryl, and mixtures thereof.

[0058] The backbones of the polymers of the present invention comprise one or more D units which are units which comprise one or more units which provide a dye transfer inhibiting benefit. The D unit can be part of the backbone itself as represented in the general formula:



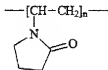
or the D unit may be incorporated into the backbone as a pendant group to a backbone unit having, for example, the formula:



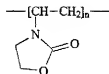
[0059] However, the number of D units depends upon the formulation. For example, the number of D units will be adjusted to provide water solubility of the polymer as well as efficacy of dye transfer inhibition. The molecular weight of the polymers of the present invention are from about 500, preferably from about 1,000, more preferably from about 10,000 to about 8,000,000, preferably to about 2,000,000, more preferably to about 1,000,000, yet more preferably to about 500,000, most preferably to about 360,000 daltons. Therefore the value of the index n is selected to provide the indicated molecular weight, and providing for a water solubility of at least 100 ppm, preferably at least about 300 ppm, and more preferably at least about 1,000 ppm in water at ambient temperature which is defined herein as 25°C.

Polymers Comprising Amide Units

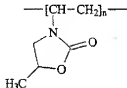
[0060] Non-limiting examples of preferred D units are D units which comprise an amide moiety. Examples of polymers wherein an amide unit is introduced into the polymer via a pendant group includes polyvinylpyrrolidone having the formula:



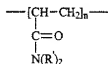
polyvinylloxazolidone having the formula:



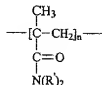
polyvinylmethyloxazolidone having the formula:



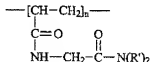
polyacrylamides and N-substituted polyacrylamides having the formula:



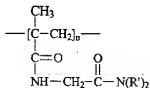
wherein each R' is independently hydrogen, C₁-C₆ alkyl, or both R' units can be taken together to form a ring comprising 4-6 carbon atoms; polymethacrylamides and N-substituted polymethacrylamides having the general formula:



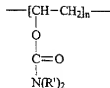
wherein each R' is independently hydrogen, C₁-C₆ alkyl, or both R' units can be taken together to form a ring comprising 4-6 carbon atoms; poly(N-acrylylglycinamide) having the formula:



wherein each R' is independently hydrogen, C₁-C₆ alkyl, or both R' units can be taken together to form a ring comprising 4-6 carbon atoms; poly(N-methacrylylglycinamide) having the formula:

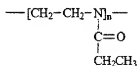


wherein each R' is independently hydrogen, C₁-C₆ alkyl, or both R' units can be taken together to form a ring comprising 4-6 carbon atoms; polyvinylurethanes having the formula:



wherein each R' is independently hydrogen, C₁-C₆ alkyl, or both R' units can be taken together to form a ring comprising 4-6 carbon atoms.

[0061] An example of a D unit wherein the nitrogen of the dye transfer inhibiting moiety is incorporated into the polymer backbone is a poly(2-ethyl-2-oxazoline) having the formula:



wherein the index n indicates the number of monomer residues present.

[0062] The amino-functional polymers of the present invention can comprise any mixture of dye transfer inhibition units which provides the product with suitable properties.

The preferred polymers which comprise D units which are amide moieties are those which have the nitrogen atoms of the amide unit highly substituted so the nitrogen atoms are in effect shielded to a varying degree by the surrounding non-polar groups. This provides the polymers with an amphiphilic character. Non-limiting examples include polyvinylpyrrolidones, polyvinylloxazolidones, N,N-disubstituted polyacrylamides, and N,N-disubstituted polymethacrylamides. A detailed description of physico-chemical properties of some of these polymers are given in "Water-Soluble Synthetic Polymers: Properties and Behavior", Philip Molyneux, Vol. 1, CRC Press, (1983) included herein by reference.

[0063] The amide containing polymers may be present partially hydrolyzed and/or crosslinked forms. A preferred polymeric compound for the present invention is polyvinylpyrrolidone (PVP). This polymer has an amphiphilic character with a highly polar amide group conferring hydrophilic and polar-attracting properties, and also has non-polar methylene and methine groups, in the backbone and/or the ring, conferring hydrophobic properties. PVP is readily soluble in aqueous and organic solvent systems. PVP is available ex ISP, Wayne, New Jersey, and BASF Corp., Parsippany, New Jersey, as a powder or aqueous solutions in several viscosity grades, designated as, e.g., K-12, K-15, K-25, and K-30. These K-values indicate the viscosity average molecular weight, as shown below:

PVP viscosity average molecular	K-12	K-15	K-25	K-30	K-60	K-90
weight (in thousands of daltons)	2.5	10	24	40	160	360

PVP K-12, K-15, and K-30 are also available ex Polysciences, Inc. Warrington, Pennsylvania, PVP K-15, K-25, and K-30 and poly(2-ethyl-2-oxazoline) are available ex Aldrich Chemical Co., Inc., Milwaukee, Wisconsin. PVP K30 (40,000) through K90 (360,000) are also commercially available ex BASF under the tradename Luviskol or commercially available ex ISP. Still higher molecular PVP like PVP 1.3MM, commercially available ex Aldrich is also suitable for use herein. Yet further PVP-type of material suitable for use in the present invention are polyvinylpyrrolidone-co-dimethylaminoethylmethacrylate, commercially available ex ISP in a quaternised form under the tradename Gafquat® or commercially available ex Aldrich Chemical Co. having a molecular weight of approximately 1.0MM; polyvinylpyrrolidone-co-vinyl acetate, available ex BASF under the tradename Luviskol®, available in vinylpyrrolidone:vinylacetate ratios of from 3:7 to 7:3; polyvinylpyrrolidone-co-vinylimidazoliumquat, commercially available ex BASF under the tradename Luviquat®.

Polymers Comprising N-oxide Units

[0064] Another D unit which provides dye transfer inhibition enhancement to the polymers described herein, are N-oxide units having the formula:



wherein R¹, R², and R³ can be any hydrocarbyl unit (for the purposes of the present invention the term "hydrocarbyl"

does not include hydrogen atom alone). The N-oxide unit may be part of a polymer, such as a polyamine, i.e., polyalkyleneimine backbone, or the N-oxide may be part of a pendant group attached to the polymer backbone. An example of a polymer which comprises an N-oxide unit as a part of the polymer backbone is polyethyleneimine N-oxide. Non-limiting examples of groups which can comprise an N-oxide moiety include the N-oxides of certain heterocycles *inter alia* pyridine, pyrrole, imidazole, pyrazole, pyrazine, pyrimidine, pyridazine, piperidine, pyrrolidine, pyrrolidone, azolidine, morpholine. A preferred polymer is poly(4-vinylpyridine N-oxide, PVNO). In addition, the N-oxide unit may be pendant to the ring, for example, aniline oxide.

[0065] N-oxide comprising polymers of the present invention will preferably have a ratio of N-oxidized amine nitrogen to non-oxidized amine nitrogen of from about 1:0 to about 1:2, preferably to about 1:1, more preferably to about 3:1.

The amount of N-oxide units can be adjusted by the formulator. For example, the formulator may co-polymerize N-oxide comprising monomers with non N-oxide comprising monomers to arrive at the desired ratio of N-oxide to non N-oxide amino units, or the formulator may control the oxidation level of the polymer during preparation. The amine oxide unit of the polyamine N-oxides of the present invention have a PK_a less than or equal to 10, preferably less than or equal to 7, more preferably less than or equal to 6. The average molecular weight of the N-oxide comprising polymers which provide a dye transfer inhibitor benefit to polymers is from about 500 daltons, preferably from about 1,000 daltons, more preferably from about 10,000 daltons to about 6,000,000 daltons, preferably to about 2,000,000 daltons, more preferably to about 360,000 daltons.

Polymers Comprising Amide Units and N-oxide Units

[0066] A further example of polymers which have dye transfer inhibition benefits are polymers which comprise both amide units and N-oxide units as described herein above. Non-limiting examples include co-polymers of two monomers wherein the first monomer comprises an amide unit and the second monomer comprises an N-oxide unit. In addition, oligomers or block polymers comprising these units can be taken together to form the mixed amide/N-oxide polymers. However, the resulting polymers must retain the water solubility requirements described herein above.

[0067] More preferably, the resin and the component capable of being co-cross-linked with the resin and/or of being amphiphilic are present in weight ratios of from 20:1 to 1:1, most preferably from 10:1 to 1:1. Within these ratio ranges, it has been found that above mentioned polymers or mixtures thereof, in combination with the polyamide-epichlorohydrin resins, show a synergistic increase performance as to the crease resistance and fabric crispness/hand on the treated fabrics.

Optionals

[0068] The composition of the invention may also comprises one or more of the following optional ingredients.

1)-Other additional fiber Lubricant

[0069] The present invention may use fiber lubricants to impart a lubricating property, or increased gliding ability, to fibers in fabric, particularly clothing. Not to be bound by theory, it is believed that water and other alcoholic solvents break, or weaken, the hydrogen bonds that hold the wrinkles in fabric, and fabric lubricants facilitate the movement of fibers with respect to one another (glide) to further release the fibers from the wrinkle condition in wet or damp fabrics. After the fabric is dried, the residual fiber lubricant, especially silicone, can provide lubricity to reduce the tendency of fabric to rewrinkle.

(a). Silicone

[0070] The present invention can use silicone, a preferred fiber lubricant, to impart a lubricating property, or increased gliding ability, to fibers in fabric, particularly clothing. Nonlimiting examples of useful silicones in the composition of the present invention include noncurable silicones such as polydimethylsilicone and volatile silicones, and curable silicones such as aminosilicones, phenylsilicones and hydroxysilicones. The word "silicone" as used herein preferably refers to water soluble as well as emulsified silicones, including those that are commercially available and those that are emulsified in the composition, unless otherwise described. Preferably, the silicones are hydrophilic; are neither irritating, toxic, nor otherwise harmful when applied to fabric or when they come in contact with human skin; are chemically stable under normal use and storage conditions; and are capable of being deposited on fabric.

[0071] A preferred class of nonionic silicone containing surfactants are the polyalkylene oxide polysiloxanes having a dimethyl polysiloxane hydrophobic moiety and one or more hydrophilic polyalkylene oxide chains, and having the general formula:



wherein a + b are from about 1 to about 50, preferably from about 1 to about 30, more preferably from about 1 to about 25, and each R1 is the same or different and is selected from the group consisting of methyl and a poly(ethyleneoxide/propyleneoxide) copolymer group having the general formula:



with at least one R1 being a poly(ethyleneoxy/propyleneoxy) copolymer group, and wherein n is 3 or 4, preferably 3; total c (for all polyalkyleneoxy side groups) has a value of from 1 to about 100, preferably from about 6 to about 100; total d is from 0 to about 14, preferably from 0 to about 3; and more preferably d is 0; total c+d has a value of from about 5 to about 150, preferably from about 7 to about 100 and each R2 is the same or different and is selected from the group consisting of hydrogen, an alkyl having 1 to 4 carbon atoms, and an acetyl group, preferably hydrogen and methyl group. Each polyalkylene oxide polysiloxane has at least one R1 group being a poly(ethyleneoxide/propyleneoxide) copolymer group.

[0072] Nonlimiting examples of this type of surfactants are the Silwet® surfactants which are available OSI Specialties Inc., a Division of Witco, Danbury, Connecticut. Representative Silwet® surfactants which contain only ethyleneoxy (C2H4O) groups are as follows.

Name	Average MW	Average a+b	Average total c
L-7608	600	1	8
L-7607	1,000	2	17
L-77	600	1	9
L-7605	6,000	20	99
L-7604	4,000	21	53
L-7600	4,000	11	68
L-7657	5,000	20	76
L-7602	3,000	20	29
L-7622	10,000	88	75

[0073] Nonlimiting examples of Silwet® surfactants which contain both ethyleneoxy (C2 H4 O) and propyleneoxy (C3 H6 O) groups are as follows.

Name	Average MW	EO/PO ratio
L-720	12,000	50/50
L-7001	20,000	40/60
L-7002	8,000	50/50
L-7210	13,000	20/80
L-7200	19,000	75/25
L-7220	17,000	20/80

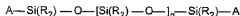
[0074] The molecular weight of the polyalkyleneoxy group (R1) is less than or equal to about 10,000. Preferably, the molecular weight of the polyalkyleneoxy group is less than or equal to about 8,000, and most preferably ranges from about 300 to about 5,000. Thus, the values of c and d can be those numbers which provide molecular weights within these ranges. However, the number of ethyleneoxy units (-C2H4O) in the polyether chain (R1) must be sufficient to render the polyalkylene oxide polysiloxane water soluble. If propyleneoxy groups are present in the polyalkyleneoxy chain, they can be distributed randomly in the chain or exist as blocks. Surfactants which contain only ethyleneoxy groups without propyleneoxy groups are preferred. Mixtures of Silwet® surfactants, in particular of Silwet surfactants which contain only propyleneoxy groups and Silwet surfactants which contain both ethyleneoxy and propyleneoxy groups, are also preferred. Preferred Silwet® surfactants are the L-7001, L-7087, L-7200, L-7280, L-7600, L-7608, L-7622, L-7657.

[0075] The preparation of polyalkylene oxide polysiloxanes is well known in the art. Polyalkylene oxide polysiloxanes of the present invention can be prepared according to the procedure set forth in U.S. Pat. No. 3,299,112, incorporated

herein by reference. Typically, polyalkylene oxide polysiloxanes of the surfactant blend of the present invention are readily prepared by an addition reaction between a hydrosiloxane (i.e., a siloxane containing silicon-bonded hydrogen) and an alkenyl ether (e.g., a vinyl, allyl, or methallyl ether) of an alkoxy or hydroxy end-blocked polyalkylene oxide). The reaction conditions employed in addition reactions of this type are well known in the art and in general involve heating the reactants (e.g., at a temperature of from about 85° C. to 110° C.) in the presence of a platinum catalyst (e.g., chloroplatinic acid) and a solvent (e.g., toluene).

[0076] Other useful silicones are volatile silicone fluids which can be cyclic silicone fluid of the formula $[(CH_3)_2SiO]_n$, where n ranges between about 3 to about 7, preferably about 5, or a linear silicone polymer fluid having the formula $(CH_3)_2SiO[(CH_3)_2SiO]_mSi(CH_3)_3$ where m can be 0 or greater and has an average value such that the viscosity at 25°C of the silicone fluid is preferably about 5 centistokes or less.

[0077] The non-volatile silicones that are useful in the composition of the present invention is polyalkyl and/or phenylsilicones silicone fluids and gums with the following structure:



[0078] The alkyl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicones remain fluid at room temperature.

[0079] Each R group preferably can be alkyl, aryl, hydroxy, or hydroxyalkyl group, and mixtures thereof, more preferably, each R is methyl, ethyl, propyl or phenyl group, most preferably R is methyl. Each A group which blocks the ends of the silicone chain can be hydrogen, methyl, methoxy, ethoxy, hydroxy, propoxy, and aryloxy group, preferably methyl. Suitable A groups include hydrogen, methyl, methoxy, ethoxy, hydroxy, and propoxy. q is preferably an integer from about 7 to about 8,000. The preferred silicones are polydimethyl siloxanes; more preferred silicones are polydimethyl siloxanes having a viscosity of from about 50 to about 1000,000 centistokes at 25°C. Mixtures of volatile silicones and non-volatile polydimethyl siloxanes are also preferred. Suitable examples include silicones offered by Dow Corning Corporation and General Electric Company.

[0080] When silicone is present, it is present at least an effective amount to provide lubrication of the fibers, typically minimum levels of wrinkle control agent included in the composition are at least about 0.025%, preferably at least about 0.05%, more preferably at least about 0.1%, even more preferably at least about 0.2%, even more highly preferably at least about 0.4%, and most preferably at least about 0.5% and typically maximum levels of wrinkle control composition are about 10%, preferably less than about 5%, more preferably less than about 3%, by weight of the usage composition.

(b). Synthetic solid particles

[0081] Solid polymeric particles of average particle size smaller than about 10 microns, preferably smaller than 5 microns, more preferably smaller than about 1 micron, e.g., Velustro® P-40 oxidized polyethylene emulsion available from Clariant, can be used as a lubricant, also Tospearl™ 105, 120, 130, 145, 240 polydimethyl siloxane polymers available from GE Silicones, since they can provide a "roller-bearing" action. When solid polymeric particles are present, they are present at an effective amount to provide lubrication of the fibers, typically from about 0.01% to about 3%, preferably from about 0.05% to about 1%, more preferably from about 0.1% to about 0.5%, by weight of the usage composition.

(c). Quaternary Ammonium Compounds

[0082] Although many quaternary ammonium compounds with alkyl substituents are suitable for this composition, quaternary ammonium compounds that contain hydrocarbon groups, including substituted groups and groups that are part of, e.g., acyl groups, which are unsaturated or branched are particularly suited for this composition. In some cases, amine precursors of the quaternary ammonium compounds can themselves be useful in this composition.

[0083] Typical levels of incorporation of the quaternary ammonium compound (active) in the wrinkle composition are of from about 0.025% to about 10% by weight, preferably from about 0.05% to about 5%, more preferably from about 0.1% to about 3%, and even more preferably from about 0.2% to about 2%, by weight of the composition, and preferably is biodegradable as disclosed hereinafter.

[0084] Suitable quaternary ammonium compounds for use in the wrinkle composition have been previously disclosed in U. S. Pat. No. 5,759,990, issued Jun. 2, 1998 in the names of E. H. Wahl, H. B. Tordill, T. Trinh, E. R. Carr, R. O. Keys, and L. M. Meyer, for Concentrated Fabric Softening Composition with Good Freeze/Thaw Recovery and Highly Unsaturated Fabric Softener Compound Therefor, and in U. S. Pat. No. 5,747,443, issued May 5, 1998 in the names of Wahl, Trinh, Gosselink, Letton, and Sivik for Fabric Softening Compound/Composition. An indicator of the suitability

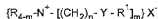
of quaternary ammonium actives for use in the compositions of the present invention is the phase transition temperature. Preferably, the phase transition temperature of the quaternary ammonium active or mixture of actives, containing less than about 5% organic solvent or water, is less than about 50°C, more preferably less than about 35°C, even more preferably less than about 20°C, and yet even more preferably less than about 10°C, or is amorphous and has no significant endothermic phase transition in the region from about -50°C to about 100°C.

[0085] The phase transition temperature can be measured with a Mettler TA 3000 differential scanning calorimeter with Mettler TC 10A Processor.

[0086] Typical suitable quaternary ammonium compounds or amine precursors are defined hereinafter.

Preferred Diester Quaternary Ammonium Active Compound (DEQA)

[0087] (1) The first type of DEQA preferably comprises, as the principal active, [DEQA (1)] compounds of the formula

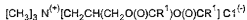


wherein each R substituent is either hydrogen, a short chain C₁-C₆, preferably C₁-C₃ alkyl or hydroxyalkyl group, e. g., methyl (most preferred), ethyl, propyl, hydroxyethyl, and the like, poly (C₂₋₃ alkoxy), preferably polyethoxy, group, benzyl, or mixtures thereof; each m is 2 or 3; each n is from 1 to about 4, preferably 2; each Y is -O-(O)C-, -C(O)-O-, -NR-C(O)-, or -C(O)-NR-; the sum of carbons in each R¹, plus one when Y is -O-(O)C- or -NR-C(O)-, is C₁₂-C₂₂, preferably C₁₄-C₂₀, with each R¹ being a hydrocarbyl, or substituted hydrocarbyl group, and X⁻ can be any quaternary ammonium-compatible anion, preferably, chloride, bromide, methylsulfate, ethylsulfate, sulfate, and nitrate, more preferably chloride or methyl sulfate (As used herein, the "percent of quaternary ammonium active" containing a given R¹ group is based upon taking a percentage of the total active based upon the percentage that the given R¹ group is, of the total R¹ groups present);

[0088] (2) A second type of DEQA active [DEQA (2)] has the formula:



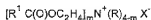
wherein each Y, R, R¹, and X⁻ have the same meanings as before. Such compounds include those having the formula:



wherein each R is a methyl or ethyl group and preferably each R¹ is in the range of C₁₅ to C₁₉. As used herein, when the diester is specified, it can include the monoester that is present. The amount of monoester that can be present is the same as in DEQA (1).

[0089] These types of agents and general methods of making them are disclosed in U.S. Pat. No. 4,137,180, Naik et al., issued Jan. 30, 1979, which is incorporated herein by reference. An example of preferred DEQA (2) is the "propyl" ester quaternary ammonium active having the formula 1,2-di(acyloxy)-3-trimethylammonio propane chloride, where the acyl is the same as that of FA¹ disclosed hereinafter.

[0090] Some preferred wrinkle compositions of the present invention contain as an essential component from about 0.025% to about 10%, preferably from about 0.05% to about 5%, more preferably from about 0.1% to about 3%, and even more preferably from about 0.2% to about 2% by weight of the composition, of quaternary ammonium active having the formula:



wherein each R¹ in a compound is a C₆-C₂₂ hydrocarbyl group, preferably having an IV from about 70 to about 140 based upon the IV of the equivalent fatty acid with the cis/trans ratio preferably being as described hereinafter, m is a number from 1 to 3 on the weight average in any mixture of compounds, each R in a compound is a C₁₋₃ alkyl or hydroxy alkyl group, the total of m and the number of R groups that are hydroxyethyl groups equaling 3, and X is a quaternary ammonium compatible anion, preferably methyl sulfate. Preferably the cis:trans isomer ratio of the fatty acid (of the C18:1 component) is at least about 1:1, preferably about 2:1, more preferably about 3:1, and even more preferably about 4:1, or higher.

[0091] These preferred compounds, or mixtures of compounds, have (a) either a Hunter "L" transmission of at least

about 85, typically from about 85 to about 95, preferably from about 90 to about 95, more preferably above about 95, if possible, (b) only low, relatively non-detectable levels, at the conditions of use, of odoriferous compounds selected from the group consisting of: isopropyl acetate; 2,2-ethylidenebis(oxy)bis-propane; 1,3,5-trioxane; and/or short chain fatty acid (4-12, especially 6-10, carbon atoms) esters, especially methyl esters; or (c) preferably, both.

[0092] The Hunter L transmission is measured by (1) mixing the quaternary ammonium active with solvent at a level of about 10% of active, to assure clarity, the preferred solvent being ethoxylated (one mole EO) 2,2,4-trimethyl-1,3-pentanediol and (2) measuring the L color value against distilled water with a Hunter ColorQUEST® colorimeter made by Hunter Associates Laboratory, Reston, Virginia.

[0093] The level of odorant is defined by measuring the level of odorant in a headspace over a sample of the quaternary ammonium active (about 92% active). Chromatograms are generated using about 200 mL of head space sample over about 2.0 grams of sample. The head space sample is trapped on to a solid absorbent and thermally desorbed onto a column directly via cryofocusing at about -100°C. The identifications of materials is based on the peaks in the chromatograms. Some impurities identified are related to the solvent used in the quaternization process, (e.g., ethanol and isopropanol). The ethoxy and methoxy ethers are typically sweet in odor. There are C₈-C₉ methyl esters found in a typical current commercial sample, but not in the typical quaternary ammonium actives of this invention. These esters contribute to the perceived poorer odor of the current commercial samples. The level of each odorant in ng/L found in the head space over a preferred active is as follows: Isopropyl acetate < 1; 1,3,5-trioxane < 5; 2,2-ethylidenebis(oxy)-bispropane < 1; C₈ methyl ester < 1; C₉ Methyl ester < 1; and C₁₀ Methyl ester < 1.

[0094] The acceptable level of each odorant is as follows: isopropyl acetate should be less than about 5, preferably less than about 3, and more preferably less than about 2, nanograms per liter (ng/L.); 2,2-ethylidenebis(oxy)-bispropane should be less than about 200, preferably less than about 100, more preferably less than about 10, and even more preferably less than about 5, nanograms per liter (ng/L.); 1,3,5-trioxane should be less than about 50, preferably less than about 20, more preferably less than about 10, and even more preferably less than about 7, nanograms per liter (ng/L.); and/or each short chain fatty acid (4-12, especially 6-10, carbon atoms) ester, especially methyl esters should be less than about 4, preferably less than about 3, and more preferably less than about 2, nanograms per liter (ng/L.).

[0095] The elimination of color and odor materials can either be accomplished after formation of the compound, or, preferably, by selection of the reactants and the reaction conditions. Preferably, the reactants are selected to have good odor and color. For example, it is possible to obtain fatty acids, or their esters, for sources of the long fatty acyl group, that have good color and odor and which have extremely low levels of short chain (C₄₋₁₂, especially C₈₋₁₀) fatty acyl groups. Also, the reactants can be cleaned up prior to use. For example, the fatty acid reactant can be double or triple distilled to remove color and odor causing bodies and remove short chain fatty acids. Additionally, the color of a triethanolamine reactant, if used, needs to be controlled to a low color level (e.g., a color reading of about 20 or less on the APHA scale). The degree of clean up required is dependent on the level of use, clarity of the product, and the presence of other ingredients. For example, adding a dye or starting with an opaque product can cover up some colors. However, for clear and/or light colored products, the color must be almost non-detectable. This is especially true as the level of the quaternary ammonium compound used in the product goes up. The degree of clean up would be especially important in products sold as concentrates that are intended for dilution by the consumer. Similarly, the odor can be covered up by higher levels of perfume, but as perfume level increases, cost associated with this approach increases too, also many consumers prefer a product with a lighter scent which precludes the approach of using higher perfume levels. Odor quality can be further improved by use of, e.g., ethanol as the quaternization reaction solvent.

[0096] Preferred biodegradable quaternary ammonium compounds comprise quaternary ammonium salt, the quaternary ammonium salt being a quaternized product of the condensation reaction between:

- a)-a fraction of saturated or unsaturated, linear or branched fatty acids, or of derivatives of said acids, said fatty acids or derivatives each possessing a hydrocarbon chain in which the number of atoms is between 5 and 21, and b)-triethanolamine,

characterized in that said condensation product has an acid value, measured by titration of the condensation product with a standard KOH solution against a phenolphthalein indicator, of less than about 6.5.

[0097] The acid value is preferably less than or equal to about 5, more preferably less than about 3.

[0098] The acid value is determined by titration of the condensation product with a standard KOH solution against a phenolphthalein indicator according to ISO#53402. The Acid Value (AV) is expressed as mg KOH/g of the condensation product.

[0099] These quaternary ammonium compounds for use herein are typically mixtures of materials. The weight percentages of compounds wherein one (monoester), two (diester), or three (triester) of the triethanolamine hydroxy groups is esterified with a fatty acyl group are as follows: Monoester - from about 12% to about 22%; diester - from about 43% to about 57%; and triester - from about 13% to about 28%. These compounds, as formed and used in the

formulation of wrinkle compositions, typically contain from about 6% to about 20% by weight of solvent, e.g., from about 3% to about 10% of a lower molecular alcohol like ethanol and from about 3% to about 10% of solvent that is more hydrophobic, like hexylene glycol.

[0100] Preferred cationic, preferably biodegradable, quaternary, ammonium compounds can contain the group $-(O)CR^1$ which is derived from animal fats, unsaturated, and polyunsaturated, fatty acids, e.g., oleic acid, and/or partially hydrogenated fatty acids, derived from vegetable oils and/or partially hydrogenated vegetable oils, such as, canola oil, safflower oil, peanut oil, sunflower oil, corn oil, soybean oil, tall oil, rice bran oil, etc. Non-limiting examples of fatty acids (FA) are listed in U.S. Pat. No. 5,759,990 at column 4, lines 45-68.

[0101] Mixtures of fatty acids, and mixtures of FAs that are derived from different fatty acids can be used, and are preferred. Nonlimiting examples of FA's that can be blended, to form FA's of this invention are as follows:

Fatty Acyl Group	FA ¹	FA ²	FA ³
C ₁₄	0	0	1
C ₁₆	3	11	25
C ₁₈	3	4	20
C14:1	0	0	0
C16:1	1	1	0
C18:1	79	27	45
C18:2	13	50	6
C18:3	1	7	0
Unknowns	0	0	3
Total	100	100	100
IV	99	125-138	56
cis/trans (C18:1)	5-6	Not Available	7
TPU	14	57	6

[0102] FA¹ is a partially hydrogenated fatty acid prepared from canola oil, FA² is a fatty acid prepared from soy bean oil, and FA³ is a slightly hydrogenated tallow fatty acid.

[0103] Preferred quaternary ammonium actives contain an effective amount of molecules containing two ester linked hydrophobic groups $[R^1C(CO)O-]$, said actives being referred to herein as "DEQA's", are those that are prepared as a single DEQA from blends of all the different fatty acids that are represented (total fatty acid blend), rather than from blends of mixtures of separate finished DEQA's that are prepared from different portions of the total fatty acid blend.

[0104] It is preferred that at least a majority of the fatty acyl groups are unsaturated, e.g., from about 50% to 100%, preferably from about 55% to about 99%, more preferably from about 60% to about 98%, and that the total level of active containing polyunsaturated fatty acyl groups (TPU) be preferably from 0% to about 30%. The cis/trans ratio for the unsaturated fatty acyl groups is usually important, with the cis/trans ratio being from about 1:1 to about 50:1, the minimum being about 1:1, preferably at least about 3:1, and more preferably from about 4:1 to about 20:1. (As used herein, the "percent of quaternary ammonium active" containing a given R¹ group is the same as the percentage of that same R¹ group is to the total R¹ groups used to form all of the quaternary ammonium actives.)

[0105] The unsaturated, including the preferred polyunsaturated, fatty acyl and/or alkylene groups, discussed hereinbefore and hereinafter, surprisingly provide good dewrinkling and effective softening, but also provide better rewetting characteristics, good antistatic characteristics, and especially, superior recovery after freezing and thawing.

[0106] These unsaturated actives are also easier to process at lower temperatures. These highly unsaturated materials (total level of active containing polyunsaturated fatty acyl groups (TPU) being typically from about 3% to about 30%, with only the low amount of solvent that normally is associated with such materials, i.e., from about 5% to about 20%, preferably from about 8% to about 25%, more preferably from about 10 to about 20%, weight of the total quaternary ammonium/solvent mixture are easier to formulate into the product and remain in stable solutions, emulsions, and or dispersions longer. This ability to process the actives at low temperatures is especially important for the polyunsaturated groups, since it minimizes degradation. Additional protection against degradation can be provided when the compounds and wrinkle compositions contain effective antioxidants, chelants, and/or reducing agents, as disclosed hereinafter.

[0107] It will be understood that substituents R and R¹ can optionally be substituted with various groups such as alkoxy or hydroxyl groups, and can be straight, or branched so long as the R¹ groups maintain their basically hydrophobic character.

[0108] A preferred long chain DEQA is the DEQA prepared from sources containing high levels of polyunsaturation, i.e., N,N-di(acyl-oxyethyl)-N,N-methylhydroxyethylammonium methyl sulfate, where the acyl is derived from fatty acids containing sufficient polyunsaturation, e.g., mixtures of tallow fatty acids and soybean fatty acids. Another preferred

long chain DEQA is the dioleil (nominally) DEQA, i.e., DEQA in which N,N-di(oleoyl-oxyethyl)-N,N-methylhydroxyethylammonium methyl sulfate is the major ingredient. Preferred sources of fatty acids for such DEQAs are vegetable oils, and/or partially hydrogenated vegetable oils, with high contents of unsaturated, e.g., oleoyl groups.

[0109] As used herein, when the DEQA diester (m=2) is specified, it can include the monoester (m=1) and/or triester (m=3) that are present. Preferably, at least about 30% of the DEQA is in the diester form, and from 0% to about 30% can be DEQA monoester, e.g., there are three R groups and one R' group.

[0110] The above compounds can be prepared using standard reaction chemistry. In one synthesis of a di-ester variation of DTDMAAC, triethanolamine of the formula $N(CH_2CH_2OH)_3$ is esterified, preferably at two hydroxyl groups, with an acid chloride of the formula $R^1C(O)Cl$, to form an amine which can be made cationic by acidification (one R is H) to be one type of active, or then quaternized with an alkyl halide, RX, to yield the desired reaction product (wherein R and R' are as defined hereinbefore). However, it will be appreciated by those skilled in the chemical arts that this reaction sequence allows a broad selection of agents to be prepared.

[0111] In preferred DEQA (1) and DEQA (2) quaternary ammonium actives, each R' is a hydrocarbyl, or substituted hydrocarbyl, group, preferably, alkyl, monounsaturated alkenyl, and polyunsaturated alkenyl groups, with the quaternary ammonium active containing polyunsaturated alkenyl groups being preferably at least about 3%, more preferably at least about 5%, more preferably at least about 10%, and even more preferably at least about 15%, by weight of the total quaternary ammonium active present; the actives preferably containing mixtures of R' groups, especially within the individual molecules.

[0112] The DEQAs herein can also contain a low level of fatty acid, which can be from unreacted starting material used to form the DEQA and/or as a by-product of any partial degradation (hydrolysis) of the quaternary ammonium active in the finished composition. It is preferred that the level of free fatty acid be low, preferably below about 15%, more preferably below about 10%, and even more preferably below about 5%, by weight of the quaternary ammonium active.

[0113] The quaternary ammonium actives herein are preferably prepared by a process wherein a chelant, preferably a diethylenetriaminepentaacetate (DTPA) and/or an ethylene diamine-N,N'-disuccinate (EDDS) is added to the process. Another acceptable chelant is tetrakis-(2-hydroxypropyl) ethylenediamine (TPED). Also, preferably, antioxidants are added to the fatty acid immediately after distillation and/or fractionation and/or during the esterification reactions and/or post-added to the finished quaternary ammonium active. The resulting active has reduced discoloration and malodor associated therewith.

[0114] The total amount of added chelating agent is preferably within the range of from about 10 ppm to about 5,000 ppm, more preferably within the range of from about 100 ppm to about 2500 ppm by weight of the formed quaternary ammonium active. The source of triglyceride is preferably selected from the group consisting of animal fats, vegetable oils, partially hydrogenated vegetable oils, and mixtures thereof. More preferably, the vegetable oil or partially hydrogenated vegetable oil is selected from the group consisting of canola oil, partially hydrogenated canola oil, safflower oil, partially hydrogenated safflower oil, peanut oil, partially hydrogenated peanut oil, sunflower oil, partially hydrogenated sunflower oil, corn oil, partially hydrogenated corn oil, soybean oil, partially hydrogenated soybean oil, tall oil, partially hydrogenated tall oil, rice bran oil, partially hydrogenated rice bran oil, and mixtures thereof. Most preferably, the source of triglyceride is canola oil, partially hydrogenated canola oil, and mixtures thereof. The process can also include the step of adding from about 0.01% to about 2% by weight of the composition of an antioxidant compound to any or all of the steps in the processing of the triglyceride up to, and including, the formation of the quaternary ammonium active.

[0115] The above processes produce a quaternary ammonium active with reduced coloration and malodor.

[0116] Additional actives that can be used herein are disclosed, at least generically for the basic structures, in U.S. Pat. Nos. 3,861,870, Edwards and Diehl; 4,308,151, Cambre; 3,886,075, Bernardino; 4,233,164, Davis; 4,401,578, Verbruggen; 3,974,076, Wiersma and Rieke; and 4,237,016, Rudkin, Clint, and Young, all of said patents being incorporated herein by reference. The additional actives herein are preferably those that are highly unsaturated versions of the traditional quaternary ammonium actives, i.e., di-long chain alkyl nitrogen derivatives, normally cationic materials, such as dioleyldimethylammonium chloride and imidazolium compounds as described hereinafter. Examples of more biodegradable fabric quaternary ammonium actives can be found in U.S. Pat. Nos. 3,408,361, Mannheimer, issued Oct. 29, 1968; 4,709,045, Kubo et al., issued Nov. 24, 1987; 4,233,451, Pracht et al., issued Nov. 11, 1980; 4,127,489, Pracht et al., issued Nov. 28, 1979; 3,669,424, Berg et al., issued Sept. 5, 1972; 4,128,485, Baumann et al., issued Dec. 5, 1978; 4,161,604, Elster et al., issued July 17, 1979; 4,189,593, Wechsler et al., issued Feb. 19, 1980; and 4,339,391, Hoffman et al., issued July 13, 1982, said patents being incorporated herein by reference.

[0117] It will be understood that suitable wrinkle compositions can include combinations of quaternary ammonium actives disclosed herein.

Anion A

[0118] In the cationic nitrogenous salts herein, the anion A⁻, which is any quaternary ammonium compatible anion, provides electrical neutrality. Most often, the anion used to provide electrical neutrality in these salts is from a strong acid, especially a halide, such as chloride, bromide, or iodide. However, other anions can be used, such as methylsulfate, ethylsulfate, acetate, formate, sulfate, carbonate, and the like. Chloride and methylsulfate are preferred herein as anion A. The anion can also, but less preferably, carry a double charge in which case A⁻ represents half a group.

[0119] In addition to lubricating fibers, quaternary ammonium compound disclosed herein can offer additional benefits including improved softening and handfeel as well as protection and/or restoration of fibers and fabric appearance.

(2) Liquid carrier

[0120] Another optional, but preferred, ingredient is a liquid carrier. The liquid carrier employed in the instant compositions is preferably at least primarily water due to its low cost, relative availability, safety, and environmental compatibility. The level of water in the liquid carrier is preferably at least about 50%, most preferably at least about 60%, by weight of the carrier. Mixtures of water and low molecular weight, e.g., <about 200, organic solvent, e.g., lower alcohols such as ethanol, propanol, isopropanol or butanol are useful as the carrier liquid. Low molecular weight alcohols include monohydric, dihydric (glycol, etc.) trihydric (glycerol, etc.), and higher polyhydric (polyols) alcohols.

(3) Dispersibility Aids

[0121] Relatively concentrated compositions containing both saturated and unsaturated diester quaternary ammonium compounds can be prepared that are stable without the addition of concentration aids. However, the compositions of the present invention may require organic and/or inorganic concentration aids to go to even higher concentrations and/or to meet higher stability standards depending on the other ingredients. These concentration aids which typically can be viscosity modifiers may be needed, or preferred, for ensuring stability under extreme conditions when particular softener active levels are used. The surfactant concentration aids are typically selected from the group consisting of (1) single long chain alkyl cationic surfactants; (2) nonionic surfactants; (3) amine oxides; (4) fatty acids; and (5) mixtures thereof. These aids are described in WO 94/20597, specifically on page 14, line 12 to page 20, line 12, which is herein incorporated by reference.

[0122] When said dispersibility aids are present, the total level is from 0.1% to 20%, preferably from 0.2% to 10%, more preferably from 0.5% to 5%, and even more preferably from 0.5% to 2% by weight of the composition. These materials can either be added as part of the active softener raw material, (I), e.g., the mono-long chain alkyl cationic surfactant and/or the fatty acid which are reactants used to form the biodegradable fabric softener active as discussed hereinbefore, or added as a separate component. The total level of dispersibility aid includes any amount that may be present as part of component (I).

[0123] Inorganic viscosity/dispersibility control agents which can also act like or augment the effect of the surfactant concentration aids, include water-soluble, ionizable salts which can also optionally be incorporated into the compositions of the present invention. A wide variety of ionizable salts can be used. Examples of suitable salts are the halides of the Group IA and IIA metals of the Periodic Table of the Elements, e.g., calcium chloride, magnesium chloride, sodium chloride, potassium bromide, and lithium chloride. The ionizable salts are particularly useful during the process of mixing the ingredients to make the compositions herein, and later to obtain the desired viscosity. The amount of ionizable salts used depends on the amount of active ingredients used in the compositions and can be adjusted according to the desires of the formulator. Typical levels of salts used to control the composition viscosity are from about 20 to about 20,000 parts per million (ppm), preferably from about 20 to about 11,000 ppm, by weight of the composition. Alkylene polyammonium salts can be incorporated into the composition to give viscosity control in addition to or in place of the water-soluble, ionizable salts above. In addition, these agents can act as scavengers, forming ion pairs with anionic detergent carried over from the main wash, in the rinse, and on the fabrics, and may improve softness performance. These agents may stabilize the viscosity over a broader range of temperature, especially at low temperatures, compared to the inorganic electrolytes.

Specific examples of alkylene polyammonium salts include L-lysine monohydrochloride and 1,5-diammonium 2-methyl pentane dihydrochloride.

(4) Stabilizers

[0124] Stabilizers can be present in the compositions of the present invention. The term "stabilizer," as used herein, includes antioxidants and reductive agents.

[0125] These agents are present at a level of from 0% to about 2%, preferably from about 0.01% to about 0.2%,

more preferably from about 0.035% to about 0.1% for antioxidants, and more preferably from about 0.01% to about 0.2% for reductive agents. These assure good odor stability under long term storage conditions for the compositions and compounds stored in molten form. The use of antioxidants and reductive agent stabilizers is especially critical for low scent products (low perfume).

[0126] Examples of antioxidants that can be added to the compositions of this invention include a mixture of ascorbic acid, ascorbic palmitate, propyl gallate, available from Eastman Chemical Products, Inc., under the trade names Tenox® PG and Tenox S-1; a mixture of BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), propyl gallate, and citric acid, available from Eastman Chemical Products, Inc., under the trade name Tenox-6; butylated hydroxytoluene, available from UOP Process Division under the trade name Sustane® BHT; tertiary butylhydroquinone, Eastman Chemical Products, Inc., as Tenox TBHQ; natural tocopherols, Eastman Chemical Products, Inc., as Tenox GT-1/GT-2; and butylated hydroxyanisole, Eastman Chemical Products, Inc., as BHA; long chain esters (C₈-C₂₂) of gallic acid, e.g., dodecyl gallate; Irganox® 1010; Irganox® 1035; Irganox® B 1171; Irganox® 1425; Irganox® 3114; Irganox® 3125; and mixtures thereof; preferably Irganox® 3125, Irganox® 1425, Irganox® 3114, and mixtures thereof; more preferably Irganox® 3125 alone. The chemical names and CAS numbers for some of the above stabilizers are listed in Table II below.

TABLE II

Antioxidant	CAS No.	Chemical Name used in Code of Federal Regulations
Irganox® 1010	6683-19-8	Tetrakis (methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)) methane
Irganox® 1035	41484-35-9	Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate
Irganox® 1098	23128-74-7	N,N'-Hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide
Irganox® B 1171	31570-04-4	
	23128-74-7	1:1 Blend of Irganox® 1098 and Irgafos® 168
Irganox® 1425	65140-91-2	Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate)
Irganox® 3114	65140-91-2	Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate)
Irganox® 3125 acid	34137-09-2	3,5-Di-tert-butyl-4-hydroxy-hydrocinnamic triester with 1,3,5-tris(2-hydroxyethyl)-S-triazine-2,4,6-(1 H, 3H, 5H)-trione
Irgafos® 168	31570-04-4	Tris(2,4-di-tert-butyl-phenyl)phosphite

[0127] Examples of reductive agents include sodium borohydride, hypophosphorous acid, Irgafos® 168, and mixtures thereof.

5- PRESERVATIVE

[0128] Optionally, but preferably, antimicrobial preservative can be added to the composition of the present invention. Contamination by certain microorganisms with subsequent microbial growth can result in an unsightly and/or malodorous solution. Because microbial growth in solutions is highly objectionable when it occurs, it is highly preferable to include an antimicrobial preservative, which is effective for inhibiting and/or regulating microbial growth in order to increase storage stability of the composition.

[0129] It is preferable to use a broad spectrum preservative, e.g., one that is effective on both bacteria (both gram positive and gram negative) and fungi. A limited spectrum preservative, e.g., one that is only effective on a single group of microorganisms, e.g., fungi, can be used in combination with a broad spectrum preservative or other limited spectrum preservatives with complementary and/or supplementary activity. A mixture of broad spectrum preservatives can also be used. In some cases where a specific group of microbial contaminants is problematic (such as Gram negatives), aminocarboxylate chelators, such as those described hereinbefore, can be used alone or as potentiators in conjunction with other preservatives. These chelators which include, e.g., ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, and other aminocarboxylate chelators, and mixtures thereof, and their salts, and mixtures thereof, can increase preservative effectiveness against Gram-negative bacteria, especially *Pseudomonas* species.

[0130] Antimicrobial preservatives useful in the present invention include biocidal compounds, i.e., substances that kill microorganisms, or biostatic compounds, i.e., substances that inhibit and/or regulate the growth of microorganisms. Well known preservatives such as short chain alkyl esters of p-hydroxybenzoic acid, commonly known as parabens; N-(4-chlorophenyl)-N'-(3,4-dichlorophenyl) urea, also known as 3,4,4'-trichlorocarbanilide or triclocarban; 2,4,4'-trichloro-2'-hydroxy diphenyl ether, commonly known as triclosan are useful preservative in the present invention.

[0131] Still other preferred preservatives are the water-soluble preservatives, i.e. those that have a solubility in water

of at least about 0.3 g per 100 ml of water, i.e., greater than about 0.3% at room temperature, preferably greater than about 0.5% at room temperature.

[0132] The preservative in the present invention is included at an effective amount. The term "effective amount" as herein defined means a level sufficient to prevent spoilage, or prevent growth of inadvertently added microorganisms, for a specific period of time. In other words, the preservative is not being used to kill microorganisms on the surface onto which the composition is deposited in order to eliminate odors produced by microorganisms. Instead, it is preferably being used to prevent spoilage of the solution in order to increase the shelf-life of the composition. Preferred levels of preservative are from about 0.0001% to about 0.5%, more preferably from about 0.0002% to about 0.2%, most preferably from about 0.0003% to about 0.1%, by weight of the usage composition.

[0133] The preservative can be any organic preservative material which will not cause damage to fabric appearance, e.g., discoloration, coloration, bleaching. Preferred water-soluble preservatives include organic sulfur compounds, halogenated compounds, cyclic organic nitrogen compounds, low molecular weight aldehydes, quaternary ammonium compounds, dehydroacetic acid, phenyl and phenolic compounds, and mixtures thereof. Non-limiting examples of preferred water-soluble preservatives for use in the present invention can be found in U.S. Patent 5,714,137, incorporated hereinbefore by reference, as well as co-pending application PCT/US 98/12154 pages 29 to 36.

[0134] Preferred water-soluble preservatives for use in the present invention are organic sulfur compounds. Some non-limiting examples of organic sulfur compounds suitable for use in the present invention are:

(a) 3-Isothiazolone Compounds

[0135] A preferred preservative is an antimicrobial, organic preservative containing 3-isothiazolone groups. This class of compounds is disclosed in U.S. Pat. No. 4,265,899, Lewis et al., issued May 5, 1981, and incorporated herein by reference. A preferred preservative is a water-soluble mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one, more preferably a mixture of about 77% 5-chloro-2-methyl-4-isothiazolin-3-one and about 23% 2-methyl-4-isothiazolin-3-one, a broad spectrum preservative available as a 1.5% aqueous solution under the trade name Kathon® CG by Rohm and Haas Company.

[0136] When Kathon® is used as the preservative in the present invention it is present at a level of from about 0.0001% to about 0.01%, preferably from about 0.0002% to about 0.005%, more preferably from about 0.0003% to about 0.003%, most preferably from about 0.0004% to about 0.002%, by weight of the composition.

[0137] Other isothiazolins include 1,2-benzisothiazolin-3-one, available under the trade name Proxel® products; and 2-methyl-4,5-trimethylene-4-isothiazolin-3-one, available under the trade name Promexal®. Both Proxel and Promexal are available from Zeneca. They have stability over a wide pH range (i.e., 4-12). Neither contain active halogen and are not formaldehyde releasing preservatives. Both Proxel and Promexal are effective against typical Gram negative and positive bacteria, fungi and yeasts when used at a level from about 0.001% to about 0.5%, preferably from about 0.005% to about 0.05%, and most preferably from about 0.01% to about 0.02% by weight of the usage composition.

(b) Sodium Pyrrithione

[0138] Another preferred organic sulfur preservative is sodium pyrrithione, with water solubility of about 50%. When sodium pyrrithione is used as the preservative in the present invention it is typically present at a level of from about 0.0001% to about 0.01%, preferably from about 0.0002% to about 0.005%, more preferably from about 0.0003% to about 0.003%, by weight of the usage composition.

[0139] Mixtures of the preferred organic sulfur compounds can also be used as the preservative in the present invention.

6- Antimicrobial active

[0140] The composition may suitably use an optional solubilized, water-soluble antimicrobial active, useful in providing protection against organisms that become attached to the treated material. The free, uncomplexed antimicrobial, e.g., antibacterial, active provides an optimum antibacterial performance.

[0141] Sanitization of fabrics can be achieved by the compositions of the present invention containing, antimicrobial materials, e.g., antibacterial halogenated compounds, quaternary compounds, and phenolic compounds.

[0142] Biguanides. Some of the more robust antimicrobial halogenated compounds which can function as disinfectants/sanitizers as well as finish product preservatives (vide infra), and are useful in the compositions of the present invention include 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with hydrochloric, acetic and gluconic acids. The digluconate salt is highly water-soluble, about 70% in water, and the diacetate salt has a solubility of about 1.8% in water. When chlorhexidine is used as a sanitizer in the present invention it is typically present at a level of from about 0.001% to about 0.4%, preferably from about 0.002%

to about 0.3%, and more preferably from about 0.01% to about 0.1%, by weight of the usage composition. In some cases, a level of from about 1% to about 2% may be needed for virucidal activity.

[0143] Other useful biguanide compounds include Cosmooc® CQ®, Vantocil® IB, including poly (hexamethylene biguanide) hydrochloride. Other useful cationic antimicrobial agents include the bis-biguanide alkanes. Usable water soluble salts of the above are chlorides, bromides, sulfates, alkyl sulfonates such as methyl sulfonate and ethyl sulfonate, phenylsulfonates such as p-methylphenyl sulfonates, nitrates, acetates, gluconates, and the like.

[0144] As stated hereinbefore, the bis biguanide of choice is chlorhexidine and its salts, e.g., digluconate, dihydrochloride, diacetate, and mixtures thereof.

[0145] Quaternary Compounds. A wide range of quaternary compounds can also be used as antimicrobial actives, in conjunction with the preferred surfactants, for compositions of the present invention that do not contain cyclodextrin. Non-limiting examples of useful quaternary compounds include: (1) benzalkonium chlorides and/or substituted benzalkonium chlorides such as commercially available Barquat® (available from Lonza), Maquat® (available from Mason), Variquat® (available from Witco/Shell), and Hyamine® (available from Lonza); (2) dialkyl quaternary such as Bardac® products of Lonza, (3) N-(3-chloroallyl) hexammonium chlorides such as Dowicide® and Dowicil® available from Dow; (4) benzethonium chloride such as Hyamine® 1622 from Rohm & Haas; (5) methylbenzethonium chloride represented by Hyamine® 10X supplied by Rohm & Haas, (6) cetylpyridinium chloride such as Cepacol chloride available from Marrell Labs. Typical concentrations for biocidal effectiveness of these quaternary compounds range from about 0.001% to about 0.8%, preferably from about 0.005% to about 0.3%, more preferably from about 0.01% to 0.2%, by weight of the usage composition. The corresponding concentrations for the concentrated compositions are from about 0.003% to about 2%, preferably from about 0.006% to about 1.2%, and more preferably from about 0.1% to about 0.8% by weight of the concentrated compositions.

[0146] Other preservatives which are conventional in the art, such as described in US 5,593, 670 incorporated herein by reference, may also be used herein.

7-Perfume

[0147] The present invention can contain a perfume. Suitable perfumes are disclosed in U.S. Pat. 5,500,138, said patent being incorporated herein by reference.

[0148] As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such as fixatives, extenders, stabilizers and solvents. These auxiliaries are also included within the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds.

[0149] Examples of perfume ingredients useful in the perfumes of the present invention compositions include, but are not limited to, hexyl cinnamic aldehyde; amyl cinnamic aldehyde; amyl salicylate; hexyl salicylate; terpineol; 3,7-dimethyl-cis-2,6-octadien-1-ol; 2,6-dimethyl-2-octanol; 2,6-dimethyl-7-octen-2-ol; 3,7-dimethyl-3-octanol; 3,7-dimethyl-trans-2,6-octadien-1-ol; 3,7-dimethyl-6-octen-1-ol; 3,7-dimethyl-1-octanol; 2-methyl-3-(para-tert-butylphenyl)-propanaldehyde; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; tricyclodecyl propionate; tricyclodecyl acetate; anisaldehyde; 2-methyl-2-(para-iso-propylphenyl)-propanaldehyde; ethyl-3-methyl-3-phenyl glycidate; 4-(para-hydroxyphenyl)-butan-2-one; 1-(2,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; para-methoxyacetophenone; para-methoxy-alpha-phenylpropene; methyl-2-n-hexyl-3-oxo-cyclopentane carboxylate; undecalactone gamma.

[0150] Additional examples of fragrance materials include, but are not limited to, orange oil; lemon oil; grapefruit oil; bergamot oil; clove oil; dodecalactone gamma; methyl-2-(2-pentyl-3-oxo-cyclopentyl) acetate; beta-naphthol methyl ether; methyl-beta-naphthylketone; coumarin; decylaldehyde; benzaldehyde; 4-tert-butylcyclohexyl acetate; alpha, alpha-dimethylphenethyl acetate; methylphenylcarbinyl acetate; Schiff's base of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate; cyclic ethyleneglycol diester of tridecanoic acid; 3,7-dimethyl-2,6-octadiene-1-nitrile; ionone gamma methyl; ionone beta; ionone alpha; pettigrain; methyl cedrylone; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene; ionone methyl; methyl-1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,5-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; benzophenone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal; 7-hydroxy-3,7-dimethyl octanol; 10-undecen-1-ol; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecan; cyclopentadecanone; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,7,8-hexamethylcyclopentane-gamma-2-benzopyrane; ambroxane; dodecylhydro-3a,6,6,9a-tetramethylnaphtho-[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; cedryl acetate; para-tert-butylcyclohexyl acetate; patchouli; oilbanum resinoid; labdanum; vetivert; copaiba balsam; fir balsam; and condensation products of: hydroxycitronellal and methyl anthranilate; hydroxycitronellal and indol; phe-

nyl acetaldehyde and indol; 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate. More examples of perfume components are: geraniol; geranyl acetate; linalool; linalyl acetate; tetrahydrolinalool; citronellol; citronellyl acetate; dihydromyrcanol; dihydromyrcenyl acetate; tetrahydromyrcenol; terpinyl acetate; nopol; nopol acetate; 2-phenylethanol; 2-phenylethyl acetate; benzyl alcohol; benzyl acetate; benzyl salicylate; benzyl benzoate; styralyl acetate; dimethylbenzylcarbinol; trichloromethylphenylcarbinyl methylphenylcarbinyl acetate; isononyl acetate; vetiveryl acetate; vetiverol; 2-methyl-3-(*p*-tert-butylphenyl)-propanal; 2-methyl-3-(*p*-isopropylphenyl)-propanal; 3-(*p*-tert-butylphenyl)-propanal; 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde; 4-acetoxy-3-pentyltetrahydropyran; methyl dihydrojasmonate; 2-n-heptylcyclopentanone; 3-methyl-2-pentyl-cyclopentanone; *n*-decanal; *n*-dodecanal; 9-decanol-1; phenoxyethyl isobutyrate; phenylacetaldehyde dimethylacetal; phenylacetaldehyde diethylacetal; geranonitrile; citronellonitrile; cedryl acetal; 3-isocampylcyclohexanol; cedryl methylether; isologifolanolone; aubepine nitrile; aubepine; heliotropine; eugenol; vanillin; diphenyl oxide; hydroxycitronellal ionones; methyl ionones; isomethyl ionones; irones; cis-3-hexenol and esters thereof; indane musk fragrances; tetralin musk fragrances; isochroman musk fragrances; macrocyclic ketones; macrolactone musk fragrances; ethylene brassylate.

[0151] The perfumes useful in the present invention compositions are substantially free of halogenated materials and nitromusks.

[0152] Suitable solvents, diluents or carriers for perfumes ingredients mentioned above are for examples, ethanol, isopropanol, diethylene glycol, monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, etc. The amount of such solvents, diluents or carriers incorporated in the perfumes is preferably kept to the minimum needed to provide a homogeneous perfume solution.

[0153] Perfume can be present at a level of from 0% to 10%, preferably from 0.1% to 5%, and more preferably from 0.2% to 3%, by weight of the finished composition. Fabric softener compositions of the present invention provide improved fabric perfume deposition.

[0154] Perfume Ingredients may also be suitably added as releasable fragrances, for example, as pro-perfumes or pro-fragrances as described in U.S. 5,652,205 Hartman et al., issued July 29, 1997, WO95/04809, WO96/02625, PCT US97/14610 filed 19 August 1997 and claiming priority of 19 August 1996, EP-A-0,752,465, co-pending application EP 96870227.0, EP 96870226.2, EP 96870026.4, and EP 96870025.6; all incorporated herein by reference.

8- Soil Release Agent

[0155] Soil Release agents are desirably used in compositions of the instant invention. Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

[0156] If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

[0157] The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 3,959,230 Hays, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; U.S. 4,000,093, Nicol, et al., issued December 28, 1976; U.S. Patent 4,702,857 Gosselink, issued October 27, 1987; U.S. 4,968,451, Scheibel et al., issued November 6; U.S. 4,702,857, Gosselink, issued October 27, 1987; U.S. 4,711,730, Gosselink et al., issued December 8, 1987; U.S. 4,721,580, Gosselink, issued January 26, 1988; U.S. 4,877,896, Maldonado et al., issued October 31, 1989; U.S. 4,956,447, Gosselink et al., issued September 11, 1990; U.S. 5,415,807 Gosselink et al., issued May 16, 1995; European Patent Application 0 219 048, published April 22, 1987 by Kud, et al.,

[0158] Further suitable soil release agents are described in U.S. 4,201,824, Violland et al.; U.S. 4,240,918 Lagasse et al.; U.S. 4,525,524 Tung et al.; U.S. 4,579,681, Ruppert et al.; U.S. 4,240,918; U.S. 4,787,989; U.S. 4,525,524; EP 279,134 A, 1988, to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N. V., 1974 all incorporated herein by reference.

[0159] Commercially available soil release agents include the METOLOSE SM100, METOLOSE SM200 manufactured by Shin-etsu Kagaku Kogyo K.K., SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (Germany), ZELCON 5126 (from Dupont) and MILEASE T (from ICI).

9-ph

[0160] An optional requirement of the compositions according to the present invention is that the pH is greater than 3, preferably between 5 and 7, more preferably in the range of 5.5 to 6.5. This range is preferred for fabric safety. When a lubricant of the diester quaternary ammonium type is used, it is most preferred to have the conventional pH

range, as measured in the neat compositions at 20 °C, of from 2.0 to 5, preferably in the range of 2.5 to 4.5, preferably about 2.5 to about 3.5. The pH of these compositions herein can be regulated by the addition of a Bronsted acid.

10- Other Optional Ingredients

[0161] The present invention can include optional components conventionally used in textile treatment compositions, for example, colorants, preservatives, bactericides, optical brighteners, opacifiers, anti-shrinkage agents, germicides, fungicides, anti-oxidants, dye fixing agent as described in EP 931133, enzymes, chelating agents, cyclodextrin as described in WO 98/56888, metallic salts to absorb amine and sulfur-containing compounds and selected from the group consisting of copper salts, zinc salts, and mixtures thereof, water-soluble polyionic polymers, e.g., water-soluble cationic polymer like polyamines, other antistatic agent, insect and/or moth repelling agents, colorants and dyes, anti-clogging agent, and the like; typical disclosure of which can be found in WO 98/56888. Still another suitable optional are void fillers like isomaltoligosaccharide mixtures, and ingredients which provide shield protection against stain like hydroxypropylcellulose as well as other cellulosic polymer like carboxymethylcellulose. The compositions are preferably free of any material that would soil or stain fabric, and are also substantially free of starch. Typically, there should be less than about 0.5%, by weight of the composition, preferably less than about 0.3%, more preferably less than about 0.1%, by weight of the composition, of starch and/or modified starch.

Form of the composition

[0162] The composition of the invention may take a variety of physical form including liquid, liquid-gel, paste-like, foam in either aqueous or non-aqueous form, powder like granular and tablet forms. A preferred form of the composition is in a liquid form.

[0163] Non-limiting forms of articles of manufactures for the dispensing of the compositions of the invention includes aerosol, spray, foam, iron as well as refill and/or cartridge for such articles.

[0164] When in a liquid form, the composition is preferably dispensed by a dispensing means such as a spray dispenser, aerosol dispenser, or refill thereof. Still another preferred dispensing means is by incorporation of the composition of the invention in the ironing tank per se, or via a cartridge preferably adapted for the iron and/or the spray dispenser.

Spray Dispenser

[0165] The present invention also relates to such compositions incorporated into a spray dispenser to create an article of manufacture that can facilitate treatment of fabric articles and/or surfaces with the compositions according to the invention at a level that is effective. The spray dispenser comprises manually activated and non-manual powered (operated) spray means and a container containing the treating composition. Typical disclosure of such spray dispenser can be found in WO 96/04940 page 19 line 21 to page 22 line 27. Preferably, the spray dispenser is selected from spray dispenser comprising battery operated pump, spray dispenser comprising a trigger spray device, spray dispenser comprising a pressurized aerosol spray dispenser.

Method of use

[0166] There is provided a method of treating fabrics, in particular to provide durable press on fabric, i.e. for providing wrinkle resistant fabrics, which comprises the steps of contacting the fabrics with a composition or a resin of the invention, as defined herein before, and subsequently curing the composition, preferably using a domestic process.

[0167] Surprisingly, it has been found that this method also provides additional benefits like a reduction of the time and/or effort involved to iron fabrics, crease resistance to fabrics, post wash wrinkle resistance, in-wear wrinkle resistance, and a reduction of the fabric aging upon multiple application.

[0168] By "contacting", it is meant any steps that is suitable for providing a contact of the composition with the fabric. This can include by soaking, washing, rinsing, and/or spraying as well as by means of a dryer sheet onto which is adsorbed the composition. Preferably, the contacting occurs after the laundering and optional drying of the fabrics, e.g. by spraying. Accordingly, in this instance, the composition of the present invention is used as an ironing aid. Still another preferred process is where the contacting occurs after the laundering and optional drying of the fabrics, e.g. by spraying, more preferably by spraying from the iron spray dispenser and/or via the vaporisation holes from the iron sole. An effective amount of the composition can be sprayed onto fabric, wherein said fabric should not be sprayed to saturation. The fabric can be cured by ironing at the normal temperature at which it should be ironed. Still another preferred way of treating the fabrics is when the fabric can be sprayed with an effective amount of the composition, allowed to dry and then ironed, or sprayed and ironed immediately.

[0169] Domestic curing of the fabric can also be caused by the heat used to dry the fabric, e.g. by tumble drying. Ironing is also particularly advantageous for curing the fabric. Without to be bound by theory, it is believed that the shorter time or the low temperatures used to domestically cure the cross-linking components mean that the fabric is more resistant to wrinkles without changing its tactile, or drape properties.

[0170] Still another advantage of the present invention is that when polyquaternary amine resins are used, such as in particular with Kymene compounds, the domestic curing can occur at room temperature, i.e. from 15 to 30°C.

[0171] Still a further advantage of the above mentioned epichlorohydrin adducts is their usability in industrial treatment. Accordingly, there is also provided a method for treating fabric which comprises the steps of contacting the fabrics with a composition of the invention, and thereafter curing the fabrics. In this preferred method, the curing is that which is conventionally known in industrial process like padding.

[0172] In a still further aspect of the invention, the composition can be sprayed onto fabrics by an in-home de-wrinkling chamber containing the fabric to be dewrinkled, thereby providing ease of operation. Conventional personal as well as industrial de-wrinkling apparatuses are suitable for use herein. Traditionally, these apparatuses act by a steaming process which effects a relaxation of the fibers. Examples of home dewrinkling chambers include shower stalls. The spraying of the composition or compounds onto the fabrics can then occur within the chamber of the apparatus or before placing the fabrics into the chamber. As for the manual method of spraying, the spraying means should preferably be capable of providing droplets with a weight average diameter of from about 8 to about 100 µm, preferably from about 10 to about 60 µm. Preferably, the loading of moisture on fabrics made of natural and synthetic fibers is from about 5 to about 25%, more preferably from about 5 to about 10% by weight of the dried fabric. Other conventional steps that can be carried out in the dewrinkling apparatus can be applied such as heating which will provide the curing step and drying. Preferably, for optimum dewrinkling benefit, the temperature profile inside the chamber ranges from about 40°C to about 80°C, more preferably from about 50°C to about 70°C. The preferred length of the drying cycle is from about 15 to about 60 minutes, more preferably from about 20 to about 45 minutes.

[0173] The steaming step in the dewrinkling apparatus can also be eliminated if the composition is maintained at a temperature range from about 22°C (about 72° F) to about 76°C (170° F) before spraying.

[0174] The present invention encompasses the method of spraying a mist of an effective amount of solution of the invention composition onto fabric and/or fabric articles. Preferably, said fabric and/or fabric articles include, but are not limited to, clothes, curtains, drapes, upholstered furniture, carpeting, bed linens, bath linens, tablecloths, sleeping bags, tents, car interiors, etc.

[0175] The compositions herein are especially useful, when used to treat garments for extending the time before another wash cycle is needed. Such garments include uniforms and other garments which are normally treated in an industrial process, which can be dewrinkled and the time between treatments extended.

[0176] Also provided herein is an article of manufacture comprising a container and the composition of the invention in association with a set of instructions to use the composition in an amount effective to provide a solution to problems involving and/or provision of a benefit related to those selected from reducing wrinkles; improving the natural drape of fabrics, imparting a crisp finish to fabrics, reducing the time and/or effort involved to iron fabrics, imparting crease resistance to fabrics, imparting post wash wrinkle resistance to fabrics, imparting in-wear resistance to fabrics, imparting a reduction of the fabric aging upon multiple application. It is important that the consumer be aware of these additional benefits, since otherwise the consumer would not know that the composition would solve these problems and/or provide these benefits.

[0177] As used herein, the phrase "in association with" means the set of instructions are either directly printed on the container itself or presented in a separate manner including, but not limited to, a brochure, print advertisement, electronic advertisement, and/or verbal communication, so as to communicate the set of instructions to a consumer of the article of manufacture. The set of instructions preferably comprises the instruction to apply an effective amount of the composition, preferably by spraying, to provide the indicated benefit, e.g. wrinkles reduction; improving the natural drape of fabrics, imparting a crisp finish to fabrics, reducing the time and/or effort involved to iron fabrics, imparting crease resistance to fabrics, imparting post wash wrinkle resistance to fabrics, imparting in-wear wrinkle resistance to fabrics, and/or imparting a reduction of the fabric aging upon multiple application.

[0178] The invention is illustrated in the following non limiting examples, in which all percentages are on a weight basis unless otherwise stated.

[0179] In the examples, the abbreviated component identifications have the following meanings:

Resin #1	Polyamide/polyamine/epichlorohydrin resin commercially available under the tradename Kymene 557H from Hercules Inc.
Resin #2	Polyamide/polyamine/epichlorohydrin resin commercially available under the tradename Kymene ULX-2 from Hercules Inc.
Resin #3	Polyamide/polyamine/epichlorohydrin resin commercially available under the tradename Luresin KNU from BASF.

Luviskol K30 Polyvinylpyrrolidone (MW about 40,000 Dalton) available from BASF.
 DC 949 Amino-functional silicone emulsion available from Dow Corning
 Silwet L7200 Polyalkylene oxide grafted polydimethylsiloxane (Ratio EO/PO : 75/25; MW 19,000) available from Witco.
 5 Silwet L7600 Polyalkylene oxide grafted polydimethylsiloxane (All EO; MW 4,000) available from Witco.
 DEG Diethyleneglycol

Example

[0180] The following are compositions according to the present invention :

	A	B	C	D	E
Resin #1	5%	4%	2.75%	-	-
Resin # 2	-	-	-	3%	-
Resin #3	-	-	-	-	5%
Luviskol K30	1%	-	2%	0.75%	0.75%
DC 949	-	2%	1.5%	0.5%	1.5%
Silwet L7200	2%	3%	1%	1.75%	1%
Silwet L7600	0.5%	1%	0.75%	0.5%	0.25%
DEG	0.25%	0.55%	0.25%	0.35%	0.55%
Perfume	0.05%	0.05%	0.05%	0.05%	0.05%
Water and Minors, e.g. preservative	Balance	Balance	Balance	Balance	Balance

Claims

1. A wrinkle reducing composition comprising:

a)-a cross-linking resin having the property of being cationic; and
 b)-a component having the property of being co-cross linkable with the resin and/or a component comprising at least one unit which provides a dye transfer inhibiting benefit;

with the proviso that when the cross-linking resin is a polyquaternary amine resins of the polyamide/polyamine/epichlorohydrin type present in an amount of 15% by weight, the amino functional polymer is not a polyethylene imine with 7 ethoxylations present in an amount of 5% by weight.

2. A composition according to Claim 1, wherein the cross-linking resin having the property of being cationic is selected from epichlorohydrin adducts of polyamine resins, polyethyleneimine resins, cationic starch, polydiallyldimethylammonium chloride, and mixtures thereof, amine-aldehyde resins, amide-aldehyde resins, and mixtures thereof.
3. The composition of Claim 1, wherein said cross-linking resin has a molecular weight between 200 and 1,000,000, preferably between 500 and 100,000.
4. A composition according to any one of Claims 1-3, wherein the cross-linking resin having the property of being cationic is present in an amount of from 0.01% to 60% by weight.
5. A composition according to any one of Claims 1-4, wherein said cross-linking resin is an aldehyde containing cross-linking resin, and wherein said composition further comprises a catalyst, preferably present in an amount of from 10% to 50%, by weight of the cross-linking components or derivative thereof.
6. A composition according to any one of Claims 1-5, wherein the component having the property of being co-cross linkable with the resin is selected from polyamine polymers, amino-functional silicones, alkyl amines, and mixtures thereof.

7. A composition according to any one of Claims 1-6, wherein the component having the property of being co-cross linkable with the resin and/or the component comprising at least one unit which provides a dye transfer inhibiting benefit is present in an amount of from 0.01 to 20% by weight of the composition.
8. A composition according to any one of Claims 1-7, wherein the composition further comprises a lubricant, preferably selected from silicones, synthetic solid particles, quaternary ammonium compounds, and mixtures thereof.
9. A composition according to any one of Claims 1-8, wherein the composition is a liquid composition, preferably a liquid aqueous composition.
10. An article of manufacture comprising a container and a composition according to any one of Claims 1-9.
11. The article of manufacture of Claim 10, wherein the article is selected from an aerosol, a spray dispenser, a refill, a cartridge, an iron, and a foam dispenser.
12. The article of manufacture of Claim 11 wherein said article is a spray dispenser selected from spray dispenser comprising battery operated pump, spray dispenser comprising a trigger spray device, spray dispenser comprising a pressurized aerosol spray dispenser, spray dispenser comprising a non-manually operated spray dispenser.
13. A method for treating the fabrics which comprises the steps of contacting the fabric with a composition according to any one of Claims 1-9 or a resin as defined in any one of Claims 1-5 and subsequently cure the fabric.
14. A method according to Claim 13, wherein said method provides a reduction of the time and/or effort involved to iron fabrics.
15. A method according to either one of Claim 13 or 14, wherein said method provides crease resistance to fabrics
16. A method according to any one of Claims 13-15, wherein said method provides post wash wrinkle resistance.
17. A method according to any one of Claims 13-16, wherein said method provides in-wear wrinkle resistance.
18. A method according to any one of Claims 13-17, wherein said method provides a reduction of the fabric aging upon multiple application.
19. A method according to any one of Claims 13-18, wherein said method is performed in an in-home dewrinkling apparatus.
20. An article of manufacture comprising a container and the composition of any one of Claims 1-9 In association with instructions to use an effective amount of said composition on fabric to provide at least one benefit selected from the group consisting of: reducing wrinkles; improving the natural drape of fabrics, imparting a crisp finish to fabrics, reducing the time and/or effort involved to iron fabrics, imparting crease resistance to fabrics, imparting post wash wrinkle resistance to fabrics, imparting in-wear wrinkle resistance to fabrics, imparting a reduction of the fabric aging upon multiple application.
21. Use of a composition as defined in Claims 1-9, or cartridge as defined in Claim 11, in an iron for treating fabrics.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 87 0222

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (INCL.7)
E,D	EP 0 978 556 A (PROCTER & GAMBLE) 9 February 2000 (2000-02-09) * page 3, line 46 - page 5, line 2 * * page 15, line 43 - page 16, line 35; examples *	1-9, 13-19,21	D06M15/11 D06M15/423 D06M15/61 C08L39/06
X,D	GB 2 185 499 A (BIP CHEMICALS LTD) 22 July 1987 (1987-07-22) * page 1, line 5 - line 55; claims *	1-4,13	
X	US 5 342 875 A (NODA ISAO) 30 August 1994 (1994-08-30) * column 3, line 60 - column 7, line 45 *	1,2	
X	EP 0 378 871 A (PROCTER & GAMBLE) 25 July 1990 (1990-07-25) * page 3, line 1 - page 5, line 19 * * claims *	1,2,4,6, 9,13-19, 21	
X	US 4 007 005 A (PATEL KANU I) 8 February 1977 (1977-02-08) * column 2, line 1 - column 4, line 9; claims *	1-6,9-12	TECHNICAL FIELDS SEARCHED (INCL.7) D06M C08L
A	WO 95 23840 A (PROCTER & GAMBLE) 8 September 1995 (1995-09-08) * the whole document *	1	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 29 March 2000	Examiner Koegler-Hoffmann, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document			

EUROPEAN PATENT OFFICE (EPO)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 99 87 0222

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

29-03-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0978556 A	09-02-2000	WO 0008127 A	17-02-2000
GB 2185499 A	22-07-1987	NONE	
US 5342875 A	30-08-1994	US 5122577 A	16-06-1992
EP 0378871 A	25-07-1990	US 4923623 A	08-05-1990
		AT 96860 T	15-11-1993
		CA 2004162 A, C	21-06-1990
		DE 68910497 D	09-12-1993
		DE 68910497 T	14-04-1994
		JP 2259167 A	19-10-1990
		JP 2831409 B	02-12-1998
		MX 172909 B	20-01-1994
US 4007005 A	08-02-1977	AU 1285676 A	13-10-1977
		CA 1085301 A	09-09-1980
		DE 2517528 A	30-12-1976
		GB 1545297 A	10-05-1979
		JP 52001043 A	06-01-1977
WO 9523840 A	08-09-1995	CN 1146779 A	02-04-1997
		JP 9509971 T	07-10-1997

EP 0978556

For more details about this annex, see Official Journal of the European Patent Office, No. 12/82

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 096 060 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

02.05.2001 Bulletin 2001/18

(51) Int Cl.7: **D06M 23/06**

(21) Application number: **99870223.7**

(22) Date of filing: **27.10.1999**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

- Hubesch, Bruno Albert Jean
3040 Neerijse-Huldenberg (BE)
- Soyez, Heidi Simonne Mariette
8400 Oostende (BE)
- Goossens, Els
2890 Oppuurs (BE)

(71) Applicant: **The Procter & Gamble Company**
Cincinnati, Ohio 45202 (US)

(74) Representative: **Gault, Nathalie et al**
BVBA Procter & Gamble Europe Sprl
Temselaan 100
1853 Strombeek-Bever (BE)

(72) Inventors:

- **Altmann, Markus W.**
1050 Brussels (BE)

(54) **Wrinkle resistant composition**

(57) There is provided a composition comprising a water-soluble lubricant and components having a devi-

ation of fabric wrinkle recovery angle versus water of at least +15, whereby the combination imparts in-wear wrinkle resistance to the fabric treated therewith.

EP 1 096 060 A1

Description

Technical field of the invention

- 5 [0001] The present invention relates to fabric care compositions and to a method for treating fabrics in order to improve various properties of fabrics, in particular in-wear wrinkle resistance.

Background of the invention

- 10 [0002] Wrinkles in textile fabrics are caused by the bending and creasing of the textile material which places an external portion of a filament in a yarn under tension while the internal portion of that filament in the yarn is placed under compression. Particularly with cotton fabrics, the hydrogen bonding that occurs between the cellulose molecules contributes to keeping wrinkles in place. The wrinkling of fabric, in particular clothing, is therefore subject to the inherent
- 15 [0003] In the modern world, with the increase of hustle and bustle and travel, there is a demand for a quick fix which will help to diminish the labor involved in home laundering and/or the cost and time involved in dry cleaning or commercial laundering. Further, it is well known that alternating cycles of using and laundering fabrics and textiles, such as articles of worn clothing and apparel, will inevitably adversely affect the appearance and integrity of the fabric and textile items so used and laundered. Fabrics and textiles simply wear out over time and with use. Laundering of fabrics
- 20 and textiles is necessary to remove soils and stains which accumulate therein and thereon during ordinary use. However, the laundering operation itself, over many cycles, can accentuate and contribute to the deterioration of the integrity and the appearance of such fabrics and textiles. Accordingly, this has brought additional pressure to bear on textile technologists to produce a product that will sufficiently reduce wrinkles in fabrics, especially clothing, whilst still producing a good appearance through a simple, convenient application of a product.
- 25 [0004] The prior art contains numerous examples of compositions for reducing wrinkles. U.S. 5,532,023, discloses aqueous wrinkle control compositions containing non-volatile silicone and film forming polymer. Preferred silicones include reactive silicones and amino-functional silicone, known as "amodimethicone". The composition containing such silicones is applied to fabric from a spray dispenser. It is found that in the spray treatment, an appreciable amount of the aqueous composition misses the fabric, and instead falls on flooring surfaces, such as rugs, carpets, concrete
- 30 floors, tiled floors, linoleum floors, bathtub floors, which leaves a silicone layer that is accumulated on and/or cured on and/or bonded to the flooring surfaces. Such silicones that are accumulated on such surfaces, and especially those that are bonded to such surfaces are difficult to remove. Flooring surfaces thus become slippery and can present a safety hazard to the household members. U.S. 5,573,695 discloses an aqueous wrinkle removal composition containing a vegetable oil based cationic quaternary ammonium surfactant, and an anionic fluorosurfactant. Similarly, U.S.
- 35 4,661,268 discloses a wrinkle removal spray comprising an aqueous alcoholic composition containing a dialkyl quaternary ammonium salt and a silicone surfactant and/or a fluoro surfactant. U.S. 5,100,566 discloses a method of reducing wrinkles in fabric by spraying the fabric with an aqueous alcoholic solution of an anionic silicate alkali metal salt. U.S. 4,906,254 discloses fabric wrinkle removal aqueous alcoholic solution containing glycerine and a nonionic surfactant. WO98/04772 provides the treatment of fabric against fabric creasing by application of a composition comprising a polycarboxylic acid or derivative thereof, and then curing the composition using a domestic process. Starch is also a conventional ingredient of dewrinkling compositions. However, while starch provides a suitable visual benefit onto the treated fabrics, it also gives fabric with an undesired stiff or starchy feeling. These patents are incorporated herein by reference.
- 40 [0005] Accordingly, the domestic treatment of fabric is a problem known in the art to the formulator of laundry compositions. Therefore, there is a need for a wrinkle reducing composition which reduces the above mentioned negatives.
- [0006] Further, most of the focus in the dewrinkling area has been on providing compositions with instant dewrinkling. However, with the current trends of reducing the labor involved in ironing, it has now been found that there is a need for a composition that would additionally provide in-wear wrinkle resistance, i.e. a composition that would provide long-lasting benefit upon ironing, and wearing.
- 50 [0007] Moreover, there is also a need for an efficient and economical composition.
- [0008] It has now surprisingly been found that the combination of a water-soluble lubricant and component having a deviation of fabric Wrinkle Recovery Angle (WRA) versus water of at least +15 fulfill such a need. This finding is particularly, especially when the component providing such deviation is a polymer. Indeed, it is known that the combination of water-soluble lubricant with polymer is often the cause of phase separation. Further, often the addition of polymer like starch on top of composition comprising water-soluble lubricant was found to give even worse results on the in-wear performance. Surprisingly, it has been found that the addition of a component providing a deviation of fabric WRA of at least +15 overcome such problems.
- 65 [0009] Accordingly, the present invention reduces wrinkles in fabrics, including clothing, dry cleanables, linens, bed

clothes, and draperies, by ironing. The present invention can be used on damp or dry clothing to relax wrinkles and give clothes a ready to wear look with lasting benefits that is demanded by today's fast paced world.

[0010] In a preferred aspect, an additional benefit of the composition of the present invention is an improved garment shape, body and crispness.

[0011] The composition of the present invention acts as an excellent ironing aid. The present invention makes the task of ironing easier and faster by creating less iron drag. The compositions of the present invention help produce a crisp, smooth appearance.

Summary of the invention

[0012] The present invention is a wrinkle reducing composition comprising a water-soluble lubricant and a component having a deviation of fabric Wrinkle Recovery angle (WRA) versus water of at least +15.

[0013] In another aspect of the invention, there is provided an article of manufacture comprising the composition of the invention.

[0014] Still in a further aspect of the invention, there is provided a method of treating fabrics for imparting benefits selected from the group consisting of: reducing wrinkles; imparting in-wear resistance to fabrics.

[0015] In a further aspect of the invention, there is provided an article of manufacture comprising a container and the composition of the invention in association with instructions to use.

Detailed description of the invention

1)-Water-soluble lubricant

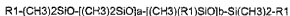
[0016] One essential component of the invention is a water-soluble lubricant. By means of this component, the composition provides an ease of ironing whilst still avoiding the staining of fabric and/or presenting safety hazard to the household members.

[0017] For the purposes of the present invention the term "water-soluble" is defined as "a component which when dissolved in water at a level of 0.2% by weight, or less, at 25° C, forms a clear, isotropic liquid".

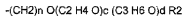
[0018] Typical water-soluble lubricants include components selected from nonionic silicone containing surfactants, sorbitan esters, ethoxylated sorbitan esters, and mixtures thereof. The water-soluble lubricants are preferably present in an amount of from 0.1% to 70% by weight of the composition, more preferably of from 1 to 10% % by weight of the composition for diluted composition and of from 20 to 50% by weight of the composition for concentrated compositions.

Nonionic Silicone Containing Surfactants

[0019] A preferred class of nonionic silicone containing surfactants are the polyalkylene oxide polysiloxanes having a dimethyl polysiloxane hydrophobic moiety and one or more hydrophilic polyalkylene side chains, and having the general formula:



wherein a + b are from about 1 to about 50, preferably from about 1 to about 30, more preferably from about 1 to about 25, and each R1 is the same or different and is selected from the group consisting of methyl and a poly(ethyleneoxide)/propyleneoxide) copolymer group having the general formula:



with at least one R1 being a poly(ethyleneoxy/propyleneoxy) copolymer group, and wherein n is 3 or 4, preferably 3; total c (for all polyalkyleneoxy side groups) has a value of from 1 to about 100, preferably from about 6 to about 100; total d is from 0 to about 14, preferably from 0 to about 3; and more preferably d is 0; total c+d has a value of from about 5 to about 150, preferably from about 7 to about 100 and each R2 is the same or different and is selected from the group consisting of hydrogen, an alkyl having 1 to 4 carbon atoms, and an acetyl group, preferably hydrogen and methyl group. Each polyalkylene oxide polysiloxane has at least one R1 group being a poly(ethyleneoxide/propyleneoxide) copolymer group.

[0020] Nonlimiting examples of this type of surfactants are the Silwet® surfactants which are available OSI Specialties Inc., a Division of Witco, Danbury, Connecticut. Representative Silwet® surfactants which contain only ethyleneoxy

(C₂H₄O) groups are as follows.

Name	Average MW	Average a+b	Average total c
L-7608	600	1	8
L-7607	1,000	2	17
L-77	600	1	9
L-7605	6,000	20	99
L-7604	4,000	21	53
L-7600	4,000	11	68
L-7657	5,000	20	76
L-7602	3,000	20	29
L-7622	10,000	88	75

[0021] Nonlimiting examples of Silwet® surfactants which contain both ethyleneoxy (C₂H₄O) and propyleneoxy (C₃H₆O) groups are as follows.

Name	Average MW	EO/PO ratio
L-720	12,000	50/50
L-7001	20,000	40/60
L-7002	8,000	50/50
L-7210	13,000	20/80
L-7200	19,000	75/25
L-7220	17,000	20/80

[0022] The molecular weight of the polyalkyleneoxy group (R₁) is less than or equal to about 10,000. Preferably, the molecular weight of the polyalkyleneoxy group is less than or equal to about 8,000, and most preferably ranges from about 300 to about 5,000. Thus, the values of c and d can be those numbers which provide molecular weights within these ranges. However, the number of ethyleneoxy units (-C₂H₄O) in the polyether chain (R₁) must be sufficient to render the polyalkylene oxide polysiloxane water soluble. If propyleneoxy groups are present in the polyalkyleneoxy chain, they can be distributed randomly in the chain or exist as blocks. Mixtures of Silwet® surfactants which contain both ethyleneoxy and propyleneoxy groups, are also preferred. Preferred Silwet® surfactants are the L-7001, L-7087, L-7200, L-7280, L-7600, L-7608, L-7622, L-7657.

[0023] The preparation of polyalkylene oxide polysiloxanes is well known in the art. Polyalkylene oxide polysiloxanes of the present invention can be prepared according to the procedure set forth in U.S. Pat. No. 3,299,112, incorporated herein by reference. Typically, polyalkylene oxide polysiloxanes of the surfactant blend of the present invention are readily prepared by an addition reaction between a hydrosiloxane (i.e., a siloxane containing silicon-bonded hydrogen) and an alkenyl ether (e.g., a vinyl, allyl, or methallyl ether) of an alkoxy or hydroxy end-blocked polyalkylene oxide). The reaction conditions employed in addition reactions of this type are well known in the art and in general involve heating the reactants (e.g., at a temperature of from about 85° C. to 110° C.) in the presence of a platinum catalyst (e.g., chloroplatinic acid) and a solvent (e.g., toluene).

[0024] Still other preferred water-soluble lubricants of the nonionic type are those from the class of sorbitan esters and/or alkyl ethoxylate sorbitan ester. These ethoxylated sorbitan esters are formed by ethoxylation of sorbitan or its cyclic derivative sorbitan, followed by esterification of one of the available hydroxy groups to introduce one long chain alkyl or alkenyl group, leaving the remaining hydroxy groups free. Compounds of this type are included in the range commercially available under the Registered Trade Mark TWEEN from Aldrich and from ICI United States Inc, but are also available from other suppliers e.g. Radasurf 7137 (Polyethoxylated (20 moles) sorbitan monolaurate), Radasurf 7147 (Polysorbate 60), Radasurf 7157 (Polysorbate 80) commercially available from FINA and Tween 65 (Polyethoxylated (20 moles) sorbitan tristearate), Tween 20 (Polyethoxylated (20 moles) sorbitan monolaurate, Tween 21 (Polyethoxylated (4 moles) sorbitan monolaurate), Tween 40 (Polyethoxylated (20 moles) sorbitan palmitate), commercially available from Aldrich.

2)-component having a deviation of fabric WRA versus water of at least +15

[0025] A component having a deviation of fabric WRA of at least +15 is another essential component of the invention. Typically, these components are present in an amount of at least about 0.01%, preferably from about 0.1% to about

20% by weight of the composition, preferably to about 4% by weight of the diluted composition, preferably to about 12% by weight of the concentrated composition.

Wrinkle Recovery Angle (WRA) Test Method:

[0026] The WRA Test method is taken from the AATCC 66-1990. This method is an American National Standard method designed for the determination of the wrinkle recovery of woven fabrics, whereby a test specimen, creased and compressed under controlled conditions of time and load, is suspended in the test instrument for a controlled recovery period, after which the recovery angle is measured. Experimental detail on how to measure this WRA is given in AATCC 66-1990, incorporated herein by reference. The WRA method is tested on 100% cotton, woven Oxford pinpoint fabric, free from wrinkles, cut in twelve specimens of 0.59 inch x 1.57 inch, six with their long dimension parallel to the warp, and six with their long dimensional parallel to the filling. The test is carried out on cloth conditioned for 24 hours at 21°C (70°F) and 65% RH. Three specimens from each set are creased on one side and three on the other. Tweezers are used to place the test specimen between the leaves of the specimen holder (2 superimposed leaves 0.63 inch wide, but of different lengths and fastened together at one end) with one end directly under the 0.71-inch mark. With the tweezers, the exposed end of the specimen is lifted over and looped back to the 0.71-inch mark on the shorter, thin metal leaf and held with the left thumbnail. The holder with the specimen is inserted into a plastic press (2 superimposed leaves of equal length (3.74 inch) and 0.79 inch wide, fastened together at one end) and a weight of 500g is applied for 5 minutes so that a crease is formed. The plastic press can then be removed and the specimen holder combination can be inserted in the tester with the exposed end of the specimen holder in the mount on the face of the tester. The crease should line up with a spot at the centre of the tester disk, and the dangling specimen leg should be lined up immediately with the vertical guide line. In order to eliminate gravitation effects, keep the dangling specimen leg aligned with the vertical guide line during the 5-min recovery period. Adjust every 15 seconds for the first minute, and once a minute thereafter. Five minutes after the removal of the creasing load, the wrinkle recovery value is read to the nearest degree from the scale. The sum is taken of the average recovery for all warp readings and all filling readings and compared with a cloth treated with water.

[0027] Components defined by their WRA are well known in the art. For example, in JAPS, Vol.15, pp.341-349 (1971) as well as in Textile Research Journal, pp. 199-201, Feb. 1970, are given various examples of components defined by a WRA, all of which are included within the scope of the present invention.

[0028] The fabric WRA obtained with the tested component is compared with the fabric WRA obtained with water, thereby giving a deviation Δ . A component which provide a Δ of at least positive(+)15, preferably having a Δ within the range of 15-30 is a component suitable for the invention.

[0029] The following represents the WRA deviation versus water of different polymers suitable for use in the present invention and according to the above procedure. In each case, numbers are arithmetic averages of 9 replicates and the results are statistically significantly different at 95% confidence level:

Polymer	Δ WRA
IMO 900	19
Avalure AC 120	21
Luviquat FC 905	15

- IMO 900: Isomaltose Oligosaccharide ex. Showa Sangyo Co.
- Avalure AC 120: Polyacrylate ex. BF Goodrich
- Luviquat FC 905: copolymer Vinylimidazolium methochloride & Vinylpyrrolidone ex. BASF

[0030] Preferred components which have a deviation of fabric WRA versus water of at least 15 are selected from shape retention polymers, polymers comprising at least one unit which provide a dye transfer inhibiting benefit, polyurethanes, polyamine polymers, Isomaltooligosaccharide, and mixtures thereof. Most preferred are the polymers which are water-soluble.

1)-Shape Retention Polymer

[0031] These polymers can be natural, or synthetic, and can act by forming a film, and/or by providing adhesive properties. E.g., the present invention can optionally use film-forming and/or adhesive polymer to impart shape retention to fabric, particularly clothing. By "adhesive" it is meant that when applied as a solution or a dispersion to a fiber surface and dried, the polymer can attach to the surface. The polymer can form a film on the surface, or when residing between

two fibers and in contact with the two fibers, it can bind the two fibers together. Other polymers such as Isomaltose Oligosaccharide can form a film and/or bond the fibers together when the treated fabric is pressed by a hot iron. Such a film will have adhesive strength, cohesive breaking strength, and cohesive breaking strain.

[0032] Nonlimiting examples for natural polymers are Isomaltose Oligosaccharide and their derivatives, and chitins and their derivatives.

[0033] The synthetic polymers useful in the present invention are comprised of monomers. Some nonlimiting examples of monomers which can be used to form the synthetic polymers of the present invention include: low molecular weight C_4 - C_6 unsaturated organic mono-carboxylic and polycarboxylic acids, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid, and mixtures thereof; esters of said acids with C_1 - C_{12} alcohols, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 1-butanol, cyclohexanol, 2-ethyl-1-butanol, neodecanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, and the like, and mixtures thereof. Nonlimiting examples of said esters are methyl acrylate, ethyl acrylate, t-butyl acrylate, methyl methacrylate, hydroxyethyl methacrylate, methoxy ethyl methacrylate, and mixtures thereof; amides and imides of said acids, such as N,N-dimethylacrylamide, N-t-butyl acrylamide, maleimides; low molecular weight unsaturated alcohols such as vinyl alcohol (produced by the hydrolysis of vinyl acetate after polymerization), allyl alcohol; esters of said alcohols with low molecular weight carboxylic acids, such as, vinyl acetate, vinyl propionate; ethers of said alcohols such as methyl vinyl ether, aromatic vinyl such as styrene, alpha-methylstyrene, 1-butylstyrene, vinyl toluene, polystyrene macromer, and the like; polar vinyl heterocyclics, such as vinyl pyrrolidone, vinyl caprolactam, vinyl pyridine, vinyl imidazole, and mixtures thereof; other unsaturated amines and amides, such as vinyl amine, diethylene triamine, dimethylaminoethyl methacrylate, ethenyl formamide; vinyl sulfonate; salts of acids and amines listed above; low molecular weight unsaturated hydrocarbons and derivatives such as ethylene, propylene, butadiene, cyclohexadiene, vinyl chloride; vinylidene chloride; and mixtures thereof and alkyl quarternized derivatives thereof, and mixtures thereof.

[0034] Preferably, said monomers are selected from the group consisting of vinyl alcohol; acrylic acid; methacrylic acid; methyl acrylate; ethyl acrylate; methyl methacrylate; t-butyl acrylate; t-butyl methacrylate; n-butyl acrylate; n-butyl methacrylate; isobutyl methacrylate; 2-ethylhexyl methacrylate; dimethylaminoethyl methacrylate; N,N-dimethyl acrylamide; N,N-dimethyl methacrylamide; N-t-butyl acrylamide; vinylpyrrolidone; vinyl pyridine; adipic acid; diethylenetriamine; salts thereof and alkyl quarternized derivatives thereof, and mixtures thereof.

[0035] Preferably, said monomers form homopolymers and/or copolymers (i.e., the film-forming and/or adhesive polymer) having a glass transition temperature (Tg) of from about -20°C to about 150°C, preferably from about -10°C to about 150°C, more preferably from about 0°C to about 100°C, most preferably, the adhesive polymer hereof, when dried to form a film will have a Tg of at least about 25°C, so that they are not unduly sticky, or "tacky" to the touch. Preferably said polymer is soluble and/or dispersible in water and/or alcohol. Said polymer typically has a molecular weight of at least about 500, preferably from about 1,000 to about 2,000,000, more preferably from about 5,000 to about 1,000,000, and even more preferably from about 30,000 to about 300,000 for some polymers.

[0036] Some non-limiting examples of homopolymers and copolymers which can be used as film-forming and/or adhesive polymers of the present invention are: adipic acid/dimethylaminohydroxypropyl diethylenetriamine copolymer; adipic acid/epoxypropyl diethylenetriamine copolymer; poly(vinylpyrrolidone/dimethylaminoethyl methacrylate); poly(vinyl alcohol); poly(vinylpyridine n-oxide); methacryloyl ethyl betaine/methacrylates copolymer; ethyl acrylate/methyl methacrylate/methacrylic acid/acrylic acid copolymer; polyamine resins; and polyquaternary amine resins; poly(ethenylformamide); poly(vinylamine) hydrochloride; poly(vinyl alcohol-co-6% vinylamine); poly(vinyl alcohol-co-12% vinylamine); poly(vinyl alcohol-co-6% vinylamine hydrochloride); and poly(vinyl alcohol-co-12% vinylamine hydrochloride). Preferably, said copolymer and/or homopolymers are selected from the group consisting of adipic acid/dimethylaminohydroxypropyl diethylenetriamine copolymer; poly(vinylpyrrolidone/dimethylaminoethyl methacrylate); poly(vinyl alcohol); ethyl acrylate/methyl methacrylate/methacrylic acid/acrylic acid copolymer; methacryloyl ethyl betaine/methacrylates copolymer; polyquaternary amine resins; poly(ethenylformamide); poly(vinylamine) hydrochloride; poly(vinyl alcohol-co-6% vinylamine); poly(vinyl alcohol-co-12% vinylamine); poly(vinyl alcohol-co-6% vinylamine hydrochloride); and poly(vinyl alcohol-co-12% vinylamine hydrochloride).

[0037] Preferred polymers useful in the present invention are selected from the group consisting of copolymers of hydrophilic monomers and hydrophobic monomers. The polymer can be linear random or block copolymers, and mixtures thereof. Such hydrophobic/hydrophilic copolymers typically have a hydrophobic monomer/hydrophilic monomer ratio of from about 85:5 to about 20:80, preferably from about 90:10 to about 40:60, more preferably from about 60:20 to about 50:50 by weight of the copolymer. The hydrophobic monomer can comprise a single hydrophobic monomer or a mixture of hydrophobic monomers, and the hydrophilic monomer can comprise a single hydrophilic monomer or a mixture of hydrophilic monomers. The term "hydrophobic" is used herein consistent with its standard meaning of lacking affinity for water, whereas "hydrophilic" is used herein consistent with its standard meaning of having affinity

for water. As used herein in relation to monomer units and polymeric materials, including the copolymers, "hydrophobic" means substantially water insoluble; "hydrophilic" means substantially water soluble. In this regard, "substantially water insoluble" shall refer to a material that is not soluble in distilled (or equivalent) water, at 25°C., at a concentration of about 0.2% by weight, and preferably not soluble at about 0.1% by weight (calculated on a water plus monomer or polymer weight basis). "Substantially water soluble" shall refer to a material that is soluble in distilled (or equivalent) water, at 25°C., at a concentration of about 0.2% by weight, and are preferably soluble at about 1% by weight. The terms "soluble", "solubility" and the like, for purposes hereof, corresponds to the maximum concentration of monomer or polymer, as applicable, that can dissolve in water or other solvents to form a homogeneous solution, as is well understood to those skilled in the art.

[0038] Nonlimiting examples of useful hydrophobic monomers are acrylic acid C_1 - C_{18} alkyl esters, such as methyl acrylate, ethyl acrylate, t-butyl acrylate; methacrylic C_1 - C_{18} alkyl esters, such as methyl methacrylate, 2-ethyl hexyl methacrylate, methoxy ethyl methacrylate; vinyl alcohol esters of carboxylic acids, such as, vinyl acetate, vinyl propionate, vinyl neodecanoate; aromatic vinyls, such as styrene, t-butyl styrene, vinyl toluene; vinyl ethers, such as methyl vinyl ether; vinyl chloride; vinylidene chloride; ethylene, propylene and other unsaturated hydrocarbons; and the like; and mixtures thereof. Some preferred hydrophobic monomers are methyl acrylate, methyl methacrylate, t-butyl acrylate, t-butyl methacrylate, n-butyl acrylate, n-butyl methacrylate, and mixtures thereof.

[0039] Nonlimiting examples of useful hydrophilic monomers are unsaturated organic mono-carboxylic and polycarboxylic acids, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid; unsaturated alcohols, such as vinyl alcohol, allyl alcohol; polar vinyl heterocyclics, such as vinyl pyrrolidone, vinyl caprolactam, vinyl pyridine, vinyl imidazole; vinyl amine; vinyl sulfonate; unsaturated amides, such as acrylamides, e.g., N, N-dimethylacrylamide, N-t-butyl acrylamide; hydroxyethyl methacrylate; dimethylaminoethyl methacrylate; salts of acids and amines listed above; and the like; and mixtures thereof. Some preferred hydrophilic monomers are acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, N,N-dimethyl methacrylamide, N-t-butyl acrylamide, dimethylamino ethyl methacrylate, vinyl pyrrolidone, salts thereof and alkyl quaternized derivatives thereof, and mixtures thereof.

[0040] Preferably, the shape retention copolymers contain hydrophobic monomers and hydrophilic monomers which comprise unsaturated organic mono-carboxylic and polycarboxylic acid monomers, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid, and salts thereof, and mixtures thereof; and optionally other hydrophilic monomers. These preferred polymers of the current invention surprisingly provide control of certain amine type malodors in fabrics, in addition to providing the fabric wrinkle control benefit. Examples of the hydrophilic unsaturated organic mono-carboxylic and polycarboxylic acid monomers are acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid, and mixtures thereof. Nonlimiting examples of the hydrophobic monomers are esters of the unsaturated organic mono-carboxylic and polycarboxylic acids cited hereinabove with C_1 - C_{12} alcohols, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol, cyclohexanol, 2-ethyl-1-butanol, and mixtures thereof, preferably methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, t-butanol, and mixtures thereof.

[0041] Compositions containing these polymers also can additionally comprise perfume, antibacterial active, odor control agent, static control agent, and mixtures thereof.

[0042] It is not intended to exclude the use of higher or lower levels of the polymers, as long as an effective amount is used to provide adhesive and film-forming properties to the composition and the composition can be formulated and effectively applied for its intended purpose.

[0043] Highly preferred adhesive and/or film forming polymers that are useful in the composition of the present invention actually contain silicone moieties in the polymers themselves. These preferred polymers include graft and block copolymers of silicone with moieties containing hydrophilic and/or hydrophobic monomers described hereinbefore. The silicone-containing copolymers in the composition of the present invention provide shape retention, body, and/or good, soft fabric feel.

[0044] Both silicone-containing graft and block copolymers useful in the present invention have the following properties:

- (1) the silicone portion is covalently attached to the non-silicone portion;
- (2) the molecular weight of the silicone portion is from about 1,000 to about 50,000; and
- (3) the non-silicone portion must render the entire copolymer soluble or dispersible in the wrinkle control composition vehicle and permit the copolymer to deposit on/adhere to the treated fabrics.

[0045] Suitable silicone copolymers include the following:

(a) Silicone Graft Copolymers

[0046] Preferred silicone-containing polymers are the silicone graft copolymers comprising acrylate groups described, along with methods of making them, in U.S. Patent No. 5,658,557, Bolich et al., issued Aug. 19, 1997, U.S. Patent No. 4,693,935, Mazurek, issued Sept. 15, 1987, and U.S. Patent No. 4,728,571, Clemens et al., issued Mar. 1, 1988. Additional silicone-containing polymers are disclosed in U.S. Pat. Nos. 5,480,634, Hayama et al., issued Oct. 2, 1996, 5,166,276, Hayama et al., issued Nov. 24, 1992, 5,061,481, issued Oct. 29, 1991, Suzuki et al., 5,106,609, Bolich et al., issued Apr. 21, 1992, 5,100,658, Bolich et al., issued Mar. 31, 1992, 5,100,657, Ansher-Jackson, et al., issued Mar. 31, 1992, 5,104,646, Bolich et al., issued Apr. 14, 1992, all of which are incorporated herein by reference.

[0047] These polymers preferably include copolymers having a vinyl polymeric backbone having grafted onto it monovalent siloxane polymeric moieties, and components consisting of non-silicone hydrophilic and hydrophobic monomers.

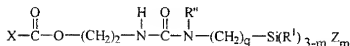
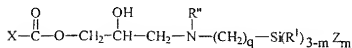
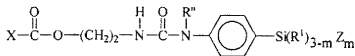
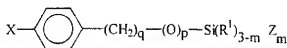
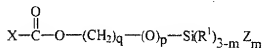
[0048] The silicone-containing monomers are exemplified by the general formula:



wherein X is a polymerizable group, such as a vinyl group, which is part of the backbone of the polymer; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl (e.g. C₁-C₄), aryl, alkaryl, alkoxy, or alkylamino; Z is a monovalent polymeric siloxane moiety having an average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3.

[0049] The preferred silicone-containing monomer has a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 3,000 to about 40,000, most preferably from about 5,000 to about 20,000.

[0050] Nonlimiting examples of preferred silicone-containing monomers have the following formulas:



[0051] In these structures m is an integer from 1 to 3, preferably 1; p is 0 or 1; q is an integer from 2 to 6; n is an integer from 0 to 4, preferably 0 or 1, more preferably 0; R¹ is hydrogen, lower alkyl, alkoxy, hydroxyl, aryl, alkylamino,

preferably R¹ is alkyl; Rⁿ is alkyl or hydrogen; X is



R³ is hydrogen or -COOH, preferably hydrogen; R⁴ is hydrogen, methyl or -CH₂COOH, preferably methyl; Z is



wherein R⁵, R⁶, and R⁷, independently are lower alkyl, alkoxy, alkylamino, hydrogen or hydroxyl, preferably alkyl; and r is an integer of from about 5 to about 700, preferably from about 60 to about 400, more preferably from about 100 to about 300. Most preferably, R⁵, R⁶, and R⁷ are methyl, p = 0, and q = 3.

[0052] Silicone-containing adhesive and/or film-forming copolymers useful in the present invention comprise from 0% to about 90%, preferably from about 10% to about 80%, more preferably from about 40% to about 75% of hydrophobic monomer, from about 0% to about 90%, preferably from about 5% to about 80% of hydrophilic monomer, and from about 5% to about 50%, preferably from about 10% to about 40%, more preferably from about 15% to about 25% of silicone-containing monomer.

[0053] The composition of any particular copolymer will help determine its formulation properties. In fact, by appropriate selection and combination of particular hydrophobic, hydrophilic and silicone-containing components, the copolymer can be optimized for inclusion in specific vehicles. For example, polymers which are soluble in an aqueous formulation preferably contain from 0% to about 70%, preferably from about 5% to about 70% of hydrophobic monomer, and from about 30% to about 98%, preferably from about 30% to about 80%, of hydrophilic monomer, and from about 1% to about 40% of silicone-containing monomer. Polymers which are dispersible preferably contain from 0% to about 70%, more preferably from about 5% to about 70%, of hydrophobic monomer, and from about 20% to about 80%, more preferably from about 20% to about 60%, of hydrophilic monomer, and from about 1% to about 40% of silicone-containing monomer.

[0054] The silicone-containing copolymers preferably have a weight average molecular weight of from about 10,000 to about 1,000,000, preferably from about 30,000 to about 300,000.

[0055] The preferred polymers comprise a vinyl polymeric backbone, preferably having a Tg or a Tm as defined above of about -20°C. and, grafted to the backbone, a polydimethylsiloxane macromer having a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably from about 7,000 to about 20,000. The polymer is such that when it is formulated into the finished composition, and then dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone. Exemplary silicone grafted polymers for use in the present invention include the following, where the composition of the copolymer is given with the approximate weight percentage of each monomer used in the polymerization reaction to prepare the copolymer: N,N-dimethylacrylamide/isobutyl methacrylate/(PDMS macromer - 20,000 approximate molecular weight) (20/60/20 w/w/w), copolymer of average molecular weight of about 400,000; N,N-dimethylacrylamide/(PDMS macromer - 20,000 approximate molecular weight) (80/20 w/w), copolymer of average molecular weight of about 300,000; and t-butylacrylate/N,N-dimethylacrylamide/(PDMS macromer - 10,000 approximate molecular weight) (70/10/20), copolymer of average molecular weight of about 400,000.

[0056] Highly preferred shape retention copolymers of this type contain hydrophobic monomers, silicone-containing monomers and hydrophilic monomers which comprise unsaturated organic mono- and polycarboxylic acid monomers, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid, and salts thereof, and mixtures thereof. These preferred polymers surprisingly provide control of certain amine type malodors in fabrics, in addition to providing the fabric wrinkle control benefit. A nonlimiting example of such copolymer is n-butylmethacrylate/acrylic acid/polydimethylsiloxane macromer, 20,000 approximate molecular weight) copolymer of average molecular weight of about 100,000, and with an approximate monomer weight ratio of about 70/10/20. A highly preferred copolymer is composed of acrylic acid, t-butyl acrylate and silicone-containing monomeric units, preferably with from about 20% to about 90%, preferably from about 30% to about 80%, more preferably from about 50% to about 75% t-butyl acrylate; from about 5% to about 60%, preferably from about 8% to about 45%, more preferably from about 10% to about 30% of acrylic acid; and from about 5% to about 50%, preferably from about 10% to about 40%, more preferably from about 15% to about 30% of polydimethylsiloxane of an average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably from about 7,000 to about 20,000. Nonlimiting examples of acrylic acid addit-t-butyl acrylate/polydimethyl siloxane macromer copolymers useful in the present invention, with approximate monomer weight ratio, are: t-butylacrylate/acrylic acid/(polydimethylsiloxane macromer, 10,000 approximate molecular weight) (70/10/20 w/w/w), copolymer of average molecular weight of about 300,000; t-butyl ac-

ylate/acrylic acid/(polydimethylsiloxane macromer, 10,000 approximate molecular weight) (63/20/17), copolymer of average molecular weight of from about 120,000 to about 150,000; and n-butylmethacrylate/acrylic acid/(polydimethylsiloxane macromer - 20,000 approximate molecular weight) (70/10/20 w/w/w), copolymer of average molecular weight of about 100,000. A useful and commercially available copolymer of this type is Diahold® ME from Mitsubishi Chemical Corp., which is a t-butyl acrylate/acrylic acid/(polydimethylsiloxane macromer, 12,000 approximate molecular weight) (60/20/20), copolymer of average molecular weight of about 128,000.

(b) Silicone Block Copolymers

[0057] Also useful herein are silicone block copolymers comprising repeating block units of polysiloxanes.

[0058] Examples of silicone-containing block copolymers are found in U.S. Patent No. 5,523,365, to Geck et al., issued June 4, 1996; U.S. Patent No. 4,889,289, to Crivello, issued Aug. 25, 1987; U.S. Patent No. 4,584,356, to Crivello, issued April 22, 1986; *Macromolecular Design, Concept & Practice*, Ed: M. K. Mishra, Polymer Frontiers International, Inc., Hopewell Jct., NY (1994), and *Block Copolymers*, A. Noshay and J. E. McGrath, Academic Press, NY (1977), which are all incorporated by reference herein in their entirety. Other silicone block copolymers suitable for use herein are those described, along with methods of making them, in the above referenced and incorporated U.S. Patent No. 5,658,577.

[0059] The silicone-containing block copolymers useful in the present invention can be described by the formulas A-B, A-B-A, and -(A-B)_n, wherein n is an integer of 2 or greater. A-B represents a diblock structure, A-B-A represents a triblock structure, and -(A-B)_n represents a multiblock structure. The block copolymers can comprise mixtures of diblocks, triblocks, and higher multiblock combinations as well as small amounts of homopolymers.

[0060] The silicone block portion, B, can be represented by the following polymeric structure



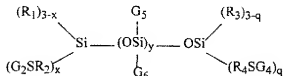
wherein each R is independently selected from the group consisting of hydrogen, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, C₂-C₆ alkylamino, styryl, phenyl, C₁-C₆ alkyl or alkoxy-substituted phenyl, preferably methyl; and m is an integer of about 10 or greater, preferably of about 40 or greater, more preferably of about 60 or greater, and most preferably of about 100 or greater.

[0061] The non-silicone block, A, comprises monomers selected from the monomers as described hereinabove in reference to the non-silicone hydrophilic and hydrophobic monomers for the silicone grafted copolymers. Vinyl blocks are preferred co-monomers. The block copolymers preferably contain one or more non-silicone blocks, and up to about 50%, preferably from about 10% to about 20%, by weight of one or more polydimethyl siloxane blocks.

(c) Sulfur-Linked Silicone-Containing Copolymers

[0062] Also useful herein are sulfur-linked silicone containing copolymers, including block copolymers. As used herein in reference to silicone containing copolymers, the term "sulfur-linked" means that the copolymer contains a sulfur linkage (i.e., -S-), a disulfide linkage (i.e., -S-S-), or a sulthydryl group (i.e., -SH).

[0063] These sulfur-linked silicone-containing copolymers are represented by the following general formula:



wherein

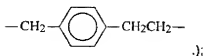
each G₅ and G₆ is independently selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, fluoroalkyl, hydrogen, and -ZSA, wherein A represents a vinyl polymers segment consisting essentially of polymerized free radically polymerizable monomer, and Z is a divalent linking group (Useful divalent linking groups Z include but are not limited to the following: C₁ to C₁₀ alkylene, alkarylene, aryene, and alkoxyalkylene. Preferably, Z is selected from the group consisting of methylene and propylene for reasons of commercial availability);

each G₂ comprises A;

each G_4 comprises A;

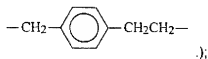
each R_1 is a monovalent moiety selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, fluoroalkyl, hydrogen, and hydroxyl (Preferably, R_1 represents monovalent moieties which can independently be the same or different selected from the group consisting of C_{1-4} alkyl and hydroxyl for reasons of commercial availability. Most preferably, R_1 is methyl.);

each R_2 is a divalent linking group (Suitable divalent linking groups include but are not limited to the following: C_1 to C_{10} alkylene, arylene, alkarylene, and alkoxyalkylene. Preferably, R_2 is selected from the group consisting of C_{1-3} alkylene and C_7-C_{10} alkarylene due to ease of synthesis of the compound. Most preferably, R_2 is selected from the group consisting of $-CH_2-$, 1,3-propylene, and



each R_3 represents monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, fluoroalkyl, hydrogen, and hydroxyl (Preferably, R_3 represents monovalent moieties which can independently be the same or different selected from the group consisting of C_{1-4} alkyl and hydroxyl for reasons of commercial availability. Most preferably, R_3 is methyl.);

each R_4 is a divalent linking group (Suitable divalent linking groups include but are not limited to the following: C_1 to C_{10} alkylene, arylene, alkarylene, and alkoxyalkylene. Preferably, R_4 is selected from the group consisting of C_{1-3} alkylene and C_7-C_{10} alkarylene for ease of synthesis. Most preferably, R_4 is selected from the group consisting of $-CH_2-$, 1,3-propylene, and



x is an integer of 0-3;

y is an integer of 5 or greater (preferably y is an integer ranging from about 14 to about 700, preferably from about 20 to about 200); and

q is an integer of 0-3;

wherein at least one of the following is true:

q is an integer of at least 1;

x is an integer of at least 1;

G_5 comprises at least one -ZSA moiety; or

G_6 comprises at least one -ZSA moiety.

[0064] As noted above, A is a vinyl polymeric segment formed from polymerized free radically polymerizable monomers. The selection of A is typically based upon the intended uses of the composition, and the properties the copolymer must possess in order to accomplish its intended purpose. If A comprises a block in the case of block copolymers, a polymer having AB and/or ABA architecture will be obtained depending upon whether a mercapto functional group -SH is attached to one or both terminal silicon atoms of the mercapto functional silicone compounds, respectively. The weight ratio of vinyl polymer block or segment, to silicone segment of the copolymer can vary. The preferred copolymers are those wherein the weight ratio of vinyl polymer segment to silicone segment ranges from about 98:2 to 50:50, in order that the copolymer possesses properties inherent to each of the different polymeric segments while retaining the overall polymer's solubility.

[0065] Sulfur linked silicone copolymers are described in more detail in U.S. Patent No. 5,468,477, to Kumar et al., issued November 21, 1995, and PCT Application No. WO 95/03776, assigned to 3M, published February 9, 1995, which are incorporated by reference herein in their entirety.

2)-Polymers comprising at least one unit which provide a dye transfer inhibiting benefit

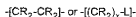
[0066] The preferred polymers comprising at least one unit which provide a dye transfer inhibiting benefit are water-soluble polymers.

[0067] The polymers comprising at least one unit which provide a dye transfer inhibiting benefit useful in the present invention have the formula:



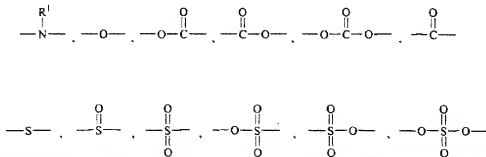
wherein the unit P is a polymer backbone which comprises units which are homopolymeric or copolymeric. D units are defined herein below. For the purposes of the present invention the term "homopolymeric" is defined as "a polymer backbone which is comprised of units having the same unit composition, i.e., formed from polymerization of the same monomer". For the purposes of the present invention the term "copolymeric" is defined as "a polymer backbone which is comprised of units having a different unit composition, i.e., formed from the polymerization of two or more monomers".

[0068] P backbones preferably comprise units having the formula:



wherein each R unit is independently hydrogen, C₁-C₁₂ alkyl, C₆-C₁₂ aryl, and D units as described herein below; preferably C₁-C₄ alkyl.

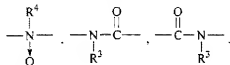
[0069] Each L unit is independently selected from heteroatom-containing moieties, non-limiting examples of which are selected from the group consisting of:



polysiloxane having the formula:



wherein the index p is from 1 to about 6; units which have dye transfer inhibition activity:



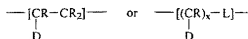
and mixtures thereof; wherein R¹ is hydrogen, C₁-C₁₂ alkyl, C₆-C₁₂ aryl, and mixtures thereof. R² is C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy, C₆-C₁₂ aryloxy, and mixtures thereof; preferably methyl and methoxy. R³ is hydrogen C₁-C₁₂ alkyl, C₆-C₁₂

aryl, and mixtures thereof; preferably hydrogen or C₁-C₄ alkyl, more preferably hydrogen. R⁴ is C₁-C₁₂ alkyl, C₆-C₁₂ aryl, and mixtures thereof.

[0070] The backbones of the polymers of the present invention comprise one or more D units which are units which comprise one or more units which provide a dye transfer inhibiting benefit. The D unit can be part of the backbone itself as represented in the general formula:



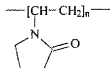
or the D unit may be incorporated into the backbone as a pendant group to a backbone unit having, for example, the formula:



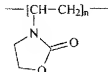
[0071] However, the number of D units depends upon the formulation. For example, the number of D units will be adjusted to provide water solubility of the polymer as well as efficacy of dye transfer inhibition. The molecular weight of the polymers of the present invention are from about 500, preferably from about 1,000, more preferably from about 10,000 most preferably from 200,000 to about 6,000,000, preferably to about 2,000,000, more preferably to about 1,000,000, yet more preferably to about 500,000, most preferably to about 360,000 daltons. Therefore the value of the index n is selected to provide the indicated molecular weight, and providing for a water solubility of at least 100 ppm, preferably at least about 300 ppm, and more preferably at least about 1,000 ppm in water at ambient temperature which is defined herein as 25°C.

Polymers Comprising Amide Units

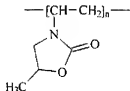
[0072] Non-limiting examples of preferred D units are D units which comprise an amide moiety. Examples of polymers wherein an amide unit is introduced into the polymer via a pendant group includes polyvinylpyrrolidone having the formula:



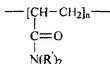
polyvinylloxazolidone having the formula:



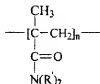
polyvinylmethyloxazolidone having the formula:



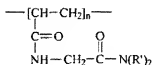
polyacrylamides and N-substituted polyacrylamides having the formula:



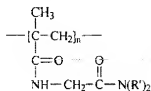
wherein each R' is independently hydrogen, C₁-C₆ alkyl, or both R' units can be taken together to form a ring comprising 4-6 carbon atoms; polymethacrylamides and N-substituted polymethacrylamides having the general formula:



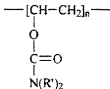
wherein each R' is independently hydrogen, C₁-C₆ alkyl, or both R' units can be taken together to form a ring comprising 4-6 carbon atoms; poly(N-acrylylglycinamide) having the formula:



wherein each R' is independently hydrogen, C₁-C₆ alkyl, or both R' units can be taken together to form a ring comprising 4-6 carbon atoms; poly(N-methacrylylglycinamide) having the formula:

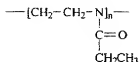


wherein each R' is independently hydrogen, C₁-C₆ alkyl, or both R' units can be taken together to form a ring comprising 4-6 carbon atoms; polyvinylurethanes having the formula:



wherein each R' is independently hydrogen, C₁-C₆ alkyl, or both R' units can be taken together to form a ring comprising 4-6 carbon atoms.

[0073] An example of a D unit wherein the nitrogen of the dye transfer inhibiting moiety is incorporated into the polymer backbone is a poly(2-ethyl-2-oxazoline) having the formula:



wherein the index n indicates the number of monomer residues present.

[0074] The amino-functional polymers of the present invention can comprise any mixture of dye transfer inhibition units which provides the product with suitable properties.

The preferred polymers which comprise D units which are amide moieties are those which have the nitrogen atoms of the amide unit highly substituted so the nitrogen atoms are in effect shielded to a varying degree by the surrounding non-polar groups. This provides the polymers with an amphiphilic character. Non-limiting examples include polyvinylpyrrolidones, polyvinylloxazolidones, N,N-disubstituted polyacrylamides, and N,N-disubstituted polymethacrylamides. A detailed description of physico-chemical properties of some of these polymers are given in "Water-Soluble Synthetic Polymers: Properties and Behavior", Philip Molyneux, Vol. I, CRC Press, (1983) included herein by reference.

[0075] The amide containing polymers may be present partially hydrolyzed and/or crosslinked forms. A preferred polymeric compound for the present invention is polyvinylpyrrolidone (PVP). This polymer has an amphiphilic character with a highly polar amide group conferring hydrophilic and polar-attracting properties, and also has non-polar methylene and methine groups, in the backbone and/or the ring, conferring hydrophobic properties. PVP is readily soluble in aqueous and organic solvent systems. PVP is available ex ISP, Wayne, New Jersey, and BASF Corp., Parsippany, New Jersey, as a powder or aqueous solutions in several viscosity grades, designated as, e.g., K-12, K-15, K-25, and K-30. These K-values indicate the viscosity average molecular weight, as shown below:

PVP viscosity average molecular weight (in thousands of daltons)	K-12	K-15	K-25	K-30	K-60	K-90
	2.5	10	24	40	160	360

PVP K-12, K-15, and K-30 are also available ex Polysciences, Inc. Warrington, Pennsylvania, PVP K-15, K-25, and K-30 and poly(2-ethyl-2-oxazoline) are available ex Aldrich Chemical Co., Inc., Milwaukee, Wisconsin. PVP K30 (40,000) through to K90 (360,000) are also commercially available ex BASF under the tradename Luviskol or commercially available ex ISP. Still higher molecular PVP like PVP 1.3MM, commercially available ex Aldrich is also suitable for use herein. Yet further PVP-type of material suitable for use in the present invention are polyvinylpyrrolidone-co-dimethylaminoethylmethacrylate, commercially available ex ISP in a quaternised form under the tradename Gafquat® or commercially available ex Aldrich Chemical Co. having a molecular weight of approximately 1.0MM; copolymer of 3-methyl-1-vinyl-1H-imidazolium chloride and 1-vinyl-2-pyrrolidone (30:70) ex BASF under the tradename Luviquat FC370, polyvinylpyrrolidone-co-vinyl acetate, available ex BASF under the tradename Luviskol®, available in vinylpyrrolidone:vinylacetate ratios of from 3:7 to 7:3; polyvinylpyrrolidone-co-vinylimidazoliumquat, commercially available ex BASF under the tradename Luviquat®.

Polymers Comprising N-oxide Units

[0076] Another D unit which provides dye transfer inhibition enhancement to the polymers described herein, are N-oxide units having the formula:



wherein R¹, R², and R³ can be any hydrocarbyl unit (for the purposes of the present invention the term "hydrocarbyl"

does not include hydrogen atom alone). The N-oxide unit may be part of a polymer, such as a polyamine, i.e., polyalkyleneamine backbone, or the N-oxide may be part of a pendant group attached to the polymer backbone. An example of a polymer which comprises an the N-oxide unit as a part of the polymer backbone is polyethyleneimine N-oxide. Non-limiting examples of groups which can comprise an N-oxide moiety include the N-oxides of certain heterocycles *inter alia* pyridine, pyrrole, imidazole, pyrazole, pyrazine, pyrimidine, pyridazine, piperidine, pyrrolidine, pyrrolidone, azolidine, morpholine. A preferred polymer is poly(4-vinylpyridine N-oxide, PVNO). In addition, the N-oxide unit may be pendant to the ring, for example, aniline oxide.

[0077] N-oxide comprising polymers of the present invention will preferably have a ratio of N-oxidized amine nitrogen to non-oxidized amine nitrogen of from about 1:0 to about 1:2, preferably to about 1:1, more preferably to about 3:1. The amount of N-oxide units can be adjusted by the formulator. For example, the formulator may co-polymerize N-oxide comprising monomers with non N-oxide comprising monomers to arrive at the desired ratio of N-oxide to non N-oxide amino units, or the formulator may control the oxidation level of the polymer during preparation. The amine oxide unit of the polyamine N-oxides of the present invention have a P_{K_a} less than or equal to 10, preferably less than or equal to 7, more preferably less than or equal to 6. The average molecular weight of the N-oxide comprising polymers which provide a dye transfer inhibitor benefit to polymers is from about 500 daltons, preferably from about 10,000 daltons, more preferably from about 20,000 daltons to about 6,000,000 daltons, preferably to about 2,000,000 daltons, more preferably to about 360,000 daltons.

Polymers Comprising Amide Units and N-oxide Units

[0078] A further example of polymers which have dye transfer inhibition benefits are polymers which comprise both amide units and N-oxide units as described herein above. Non-limiting examples include co-polymers of two monomers wherein the first monomer comprises an amide unit and the second monomer comprises an N-oxide unit. In addition, oligomers or block polymers comprising these units can be taken together to form the mixed amide/N-oxide polymers.

[0079] However, the resulting polymers must retain the water solubility requirements described herein above.

3)-Urethanes polymers

[0080] Polymers of the urethane type are also suitable components for use herein. A typical disclosure of polyurethane polymer can be found in EP844274A1 as well as in EP839903.

4)-Isomaltooligosaccharide

[0081] Isomaltooligosaccharides (IMO) (including mixtures), the individual components of said mixtures, substituted versions thereof, derivatised versions thereof, and mixtures thereof are suitable components for use herein. Currently IMO is used as corn syrup. These components are particularly suitable where cellulosic fibers/fabrics are used, such as cotton, rayon, ramie, jute, flax, linen, polymeric-fibers, Lyocell (Tencel®), polyester/cotton blends, other cotton blends, and the like, especially cotton, rayon, linen, polyester/cotton blends, and mixtures thereof.

[0082] Suitable fabric improving actives that are useful in the present invention include oligosaccharides with a degree of polymerization (DP) of from about 1 to about 15, preferably from about 2 to about 10, and wherein each monomer is selected from the group consisting of reducing saccharide containing 5 and/or 6 carbon atoms, including isomaltose, isomaltotriose, isomaltotetraose, isomaltooligosaccharide, fructooligosaccharide, levoglucosaccharides, galactooligosaccharide, xylooligosaccharide, gentiooligosaccharides, disaccharides, glucose, fructose, galactose, xylose, mannose, arabinose, rhamnose, maltose, sucrose, lactose, maltulose, ribose, lyxose, allose, altrose, gulose, idose, talose, trehalose, nigerose, kojibiose, lactulose, oligosaccharides, maltoligosaccharides, trisaccharides, tetrasaccharides, pentasaccharides, hexasaccharides, oligosaccharides from partial hydrolysates of natural polysaccharide sources, and the like, and mixtures thereof, preferably mixtures of isomaltooligosaccharides, especially mixtures including isomaltooligosaccharides, comprising from about 3 to about 7 units of glucose, respectively, and which are linked by 1,2- α , 1,3- α , 1,4- α - and 1,6- α -linkages, and mixtures of these linkages. Oligosaccharides containing β -linkages are also preferred. Preferred oligosaccharides are acyclic and have at least one linkage that is not an α -1,4-glycosidic bond. A preferred oligosaccharide is a mixture containing IMO: from 0 to about 20 % by weight of glucose, from about 10 to about 85 % of isomaltose, from about 1 % to about 45 % of each of isomaltotriose, isomaltotetraose and isomaltopentaose, from 0 to about 3 % of each of isomaltohexaose, isomaltoheptaose, isomaltooctaose and isomaltononaose, from about 0.2 % to about 15 % of each of isomaltohexaose and isomaltoheptaose, and from 0 to about 50 % by weight of said mixture being isomaltooligosaccharides of 2 to 7 glucose units and from 0 to about 10 % by weight of said mixture being isomaltooligosaccharides of about 7 to about 10 glucose units. Other nonlimiting examples of preferred acyclic oligosaccharides, with approximate content by weight percent, are:

Isomaltoligosaccharide Mixture I	
Trisaccharides (maltotriose, panose, isomaltotriose)	40-65%
Disaccharides (maltose, isomaltose)	5-15%
Monosaccharide (glucose)	0-20%
Higher branched sugars (4 < DP < 10)	10-30%

Isomaltoligosaccharide Mixture II	
Trisaccharides (maltotriose, panose, isomaltotriose)	10-25%
Disaccharides (maltose, isomaltose)	10-55%
Monosaccharide (glucose)	10-20%
Higher branched sugars (4 < DP < 10)	5-10%

Isomaltoligosaccharide Mixture III	
Tetrasaccharides (stachyose)	10-40%
Trisaccharides (raffinose)	0-10%
Disaccharides (sucrose, trehalose)	10-50%
Monosaccharide (glucose, fructose)	0-10%
Other higher branched sugars (4 < DP < 10)	0 - 5%

[0083] Oligosaccharide mixtures are either prepared by enzymatic reactions or separated as natural products from plant materials. The enzymatic synthesis of oligosaccharides involves either adding monosaccharides, one at a time, to a di- or higher saccharide to produce branched oligosaccharides, or it can involve the degradation of polysaccharides followed by transfer of saccharides to branching positions. For instance, Oligosaccharide Mixtures I and II are prepared by enzymatic hydrolysis of starch to maltoligosaccharides, which are then converted to isomaltoligosaccharides by a transglucosidase reaction. Oligosaccharide Mixture III, for example, is a mixture of oligosaccharides isolated from soybean. Soybean oligosaccharides such as Mixture III, are of pure natural origin.

[0084] Substituted and/or derivatised materials of the oligosaccharides listed hereinabove are also suitable in the present invention. Nonlimiting examples of these materials include: carboxyl and hydroxymethyl substitutions (e.g., glucuronic acid instead of glucose); amino oligosaccharides (amine substitution, e.g., glucosamine instead of glucose); cationic quaternized oligosaccharides; C₁-C₆ alkylated oligosaccharides; acetylated oligosaccharide ethers; oligosaccharides having amino acid residues attached (small fragments of glycoprotein); oligosaccharides containing silicone moieties. These substituted and/or derivatised oligosaccharides can provide additional benefits, such as: carboxyl and hydroxymethyl substitutions can introduce readily oxidizable materials on and in the fiber, thus reducing the probability of the fiber itself being oxidized by oxidants, such as bleaches; amine substitution can bind and/or condense with oxidatively damaged regions of the fiber to rejuvenate aged fabrics; acetylated sugar ethers can serve as bleach activators in subsequent processes where hydrogen peroxide is present; oligosaccharides having amino acid residues can improve delivery of fabric care benefits for fabrics containing proteinaceous fibers, e.g., wool and silk; and silicone-derivatised oligosaccharides can provide additional fabric softness and lubricity. C₆ alkyl oligosaccharide is disclosed (along with other higher, viz., C₈-C₃₀, alkyl polysaccharides) in U.S. Pat. 4,565,647. Typical disclosure of C₁-C₆ alkylated oligosaccharides can also be found in U.S. 4,488,981. These patents are incorporated herein by reference.

[0085] One preferred isomaltoligosaccharide is IMO 900 commercially available from Showa Sangyo Co.)

5)- Polyvinylamines polymers

[0086] Polyvinylamines polymers are also suitable component giving a deviation of fabric WRA of at least 15. Typical polyvinylamines polymers include the the quaternized and non-quaternized polyvinylamines having the formula:



wherein R is hydrogen, C1-C12 linear or branched alkyl, benzyl, or alkyleneoxy having the formula (R10)zY, wherein R1 is C1-C6 linear or branched alkylene, Y is hydrogen or an anionic unit, non-limiting examples of which include, - (CH2)fCO2M, -C(O)(CH2)fCO2M, -(CH2)fPO3M, -(CH2)fSO3M, -(CH2)(CHSO3M)-(CH2)fSO3M, -(CH2)(CHSO2M)(CH2)fSO3M, -C(O)CH2CH(SO3M)CO2M, -C(O)CH2CH(CO2M)NHCH(CO2M)CH2CO2M, -C(O)CH2CH(CO2M)NHCH2CO2M, -CH2CH(OZ)CH2O(R10)IZ, -(CH2)CH[O(R20)IZ]CH2O(R20)IZ, and mixtures thereof, wherein Z is hydrogen or an anionic unit non-limiting examples of which include -(CH2)fCO2M, -C(O)(CH2)fCO2M, -(CH2)fPO3M, -(CH2)fOPO3M, -(CH2)fSO3M, -(CH2)(CHSO3M)-(CH2)fSO3M, -(CH2)(CHSO2M)(CH2)fSO3M, -C(O)CH2CH(SO3M)CO2M, -C(O)CH2CH(CO2M)NHCH(CO2M)CH2CO2M, and mixtures thereof, M is a cation which provides charge neutrality; and the index f is from 0 to 6, t is 0 or 1, z is from 1 to 50.

The index x has the value from about 50 to about 1,500; preferably the index x has a value such that the resulting polymeric suds stabilizer has an average molecular weight of from about 2,500, preferably from about 10,000, more preferably from about 20,000 to about 150,000, preferably to about 90,000, more preferably to about 80,000 daltons. [0087] Most preferred polymers for use in the present invention are water-soluble, including IMO 900 (Isomaltose Oligosaccharide ex. Showa Sangyo Co.), Avalure AC 120 (Polyacrylate ex. BF Goodrich), Luviskol K30, K60 and K85 (Polyvinylpyrrolidone MW 40,000, 400,000 and 1,250,000 ex. BASF), Luvitec VPC 55K65W (copolymer Vinylpyrrolidone & Vinylcaprolactam ex. BASF), Luvitec Quat 73W (copolymer 1-methyl-3-vinylimidazolium-methylsulfate & 1-vinyl-2-pyrrolidone ex. BASF), Luviquat FC 905 (copolymer Vinylimidazolium methochloride & Vinylpyrrolidone ex. BASF), Sedipur 520 (modified Polyacrylamide ex. BASF), Chitanide 222 (Chitosan succinamide ex. MIP), Mirasil ADM-E (Aminodimethicone ex. Rhone-Poulenc), Percol 370 (diallyl amine polymer ex. CIBA), Amphomer HC (Acrylate / Octylacrylamide copolymer ex. National Starch), and mixtures thereof.

[0088] More preferably, the water-soluble lubricant and the component, preferably polymer, having a deviation of fabric WRA of at least +15 are present in weight ratios of water-soluble lubricant to component of from 10:1 to 1:1. Indeed, it has been found that within these ratio ranges the resulting composition provides best in wear wrinkle benefit.

Optionals

[0089] The composition of the invention may also comprises one or more of the following optional ingredients.

1)- Durable press polymer

[0090] Durable press polymers are optional components of the invention. These polymers can be a cross-linking resin having the property of being cationic. By "cross-linking resin having the property of being cationic", it is meant that the resin is at least partially positively charged. It is not however necessary that the reactive part of the molecule carries the positive charge. Indeed, polymeric resins can be based on positively charged monomers which help the deposition on the fibers.

[0091] Cross-linking resins having the property of being cationic suitable for use herein are those commonly known as having wet strength in the paper field. At least two mechanisms have been postulated to account for the mechanism by which wet strength resin act. One is that wet strength resins form covalent bonds between adjacent fibers while another is that the wet strength resin places a layer over the hydrogen bonds formed between adjacent paper fibers and thus prevents water from breaking the hydrogen bonds.

[0092] Conventional wet-strength agents suitable for use herein include compounds made of epichlorohydrin adducts of polyamine resins, polyethylenimine resins, cationic starch, polydiallyldimethylammonium chloride, and mixtures thereof, amine-aldehyde resins such as melamine-formaldehyde resin, amide-aldehyde resins, and mixtures thereof. For use within the meaning of the present invention, there can also be used materials of the above-mentioned classes of substances which admittedly do not themselves possess any outstanding wet-strength properties but, nevertheless, have the same durable press effect as do the wet-strength agents as described therein.

[0093] Among the class of epichlorohydrin adducts of polyamine resins, polyethylenimine resins, cationic starch, polydiallyldimethylammonium chloride, and mixtures thereof, the preferred components are the polymeric amine-epichlorohydrin resins selected from the group consisting of a polyamide-epichlorohydrin (PAE) resin, a polyallylenepolyamine-epichlorohydrin (PAPAE) resin, and an amine polymer-epichlorohydrin (APE) resin, in which the amine groups have been alkylated with epichlorohydrin to produce a polyamine-epichlorohydrin resin that has azetidinium or epoxide

functionality. Preferably, for use herein, the cross-linking resin having cationic properties is a cationic wet strength resin that is produced by reacting a saturated aliphatic dicarboxylic acid containing three to ten carbon atoms with a polyalkylenepolyamine, containing from two to four ethylene groups, two primary amine groups, and one to three secondary amine groups (such as diethylenetriamine, triethylenetetramine and tetraethylenepentamine), to form a poly(aminoamide) having secondary amine groups that are alkylated with epichlorohydrin to form a PAE resin.

[0094] These polyamide/polyamine/epichlorohydrin wet-strength resins are fully described by Carr, Doane, Hamerstrand and Hofreiter, in an article appearing in the Journal of Applied Polymer Science Vol. 17, pp. 721-735 (1973). Such resins are available as KYMENE from Hercules, Inc. A commercial synthesis of such resins from adipic acid, diethylene triamine and epichlorohydrin is described in the Carr et al publication, *ibid.*, and is U.S. Pat. No. 2,926,154 (Feb. 23, 1960) to G. I. Keim or US 4,240,995. Reference can be made to these publications for further details regarding the preparation of polyamide/polyamine/epichlorohydrin resins.

[0095] Most preferred cross-linking resin having cationic properties from this class are the wet strength resin Kymene 557H (available from Hercules Incorporated), in which adipic acid is reacted with diethylenetriamine to form a poly (aminoamide) that is alkylated and crosslinked with epichlorohydrin to form a PAE resin. Still another preferred cross-linking resin having cationic properties made of epichlorohydrin are Luresin, RTM and Etadurin which both are polyamidoamine-epichlorohydrin resins.

[0096] Amine-aldehyde resins are suitable cross-linking resins for the present invention and are made by condensation of amine or amide monomers with aldehydes such as formaldehyde or glyoxal. Preferred amines are those having low molecular weight amines e.g. melamine or polymeric amines e.g. poly-diallylamine, preferably quarternized. Preferred amides are those polymeric amides such as polyacrylamide. All these suitable amine/amide monomers can also be copolymerized with cationic monomers.

[0097] Among the class of amine-aldehyde cross-linking resin, preferred are those from the class of melamine-formaldehyde resin. Melamine-formaldehyde resins of this type are known as crosslinking agents of this type in the coating industry and are also described, for example, in German Auslegeschrift Nos. 2,457,387 (U.S. Pat. No. 4,035,213 incorporated herein by reference) and 1,719,324 and, in particular, in U.S. Pat. No. 3,242,230 incorporated herein by reference.

[0098] Preferred melamine-formaldehyde resin are those commercially available under the tradenames Madurit, and Cassurit from Clariant.

[0099] Still other preferred cross-linking resin having the property of being cationic among the class of amine-aldehyde cross-linking resin are the Poly(acrylamide-glyoxal) resin commercially available under the tradename SOLIDURIT KM from Clariant.

[0100] According to the present invention, there can also be used a mixture of wet-strength agents of the above-mentioned types or equivalent compounds.

[0101] Preferably for the purpose of the invention, the cross-linking resin having cationic properties have a molecular weight between 200 and 1,000,000, preferably between 500 and 100,000, most preferably between 1000 and 25,000. Cross-linking resin having a low molecular weight are most preferred for use in the present invention as they are more water-soluble and have a better fiber penetration. By low molecular weight it is meant a molecular weight within the range of from 25 to 2000, preferably from 50 to 1000, and more preferably from 50 to 500.

[0102] It is desirable if the level of cross-linking components or derivative thereof is present in an amount of from 0.01% to 60%, preferably from 0.01% to 30% by weight of the total composition.

[0103] It is advantageous for aldehyde containing cross-linking resins if a catalyst is used with compositions of the invention. Preferred catalysts includes organic acids such as citric acid, succinic acid, and tartaric acids, as well as conventional Lewis acid such as $AlCl_3$ or $MgCl_2$, or salts thereof, or mixtures thereof. A typical example of catalyst is the catalyst NKD made of a mixture of salts and organic acid, and commercially available from Hoechst.

[0104] It is preferred if the level of catalyst is from 10% to 50%, preferably from 20 to 40% by weight of the cross-linking components or derivative thereof.

[0105] For other cross-linking resins like the Kymene, the use of a catalyst is not necessary.

(2) Liquid carrier

[0106] Another optional, but preferred, ingredient is a liquid carrier. The liquid carrier employed in the instant compositions is preferably at least primarily water due to its low cost, relative availability, safety, and environmental compatibility. The level of water in the liquid carrier is preferably at least about 50%, most preferably at least about 60%, by weight of the carrier. Mixtures of water and low molecular weight, e.g., <about 200, organic solvent, e.g., lower alcohols such as ethanol, propanol, isopropanol or butanol are useful as the carrier liquid. Low molecular weight alcohols include monohydric, dihydric (glycol, etc.) trihydric (glycerol, etc.), and higher polyhydric (polyols) alcohols.

(3) Dispersibility Aids

[0107] Relatively concentrated compositions containing both saturated and unsaturated diester quaternary ammonium compounds can be prepared that are stable without the addition of concentration aids. However, the compositions of the present invention may require organic and/or inorganic concentration aids to go to even higher concentrations and/or to meet higher stability standards depending on the other ingredients. These concentration aids which typically can be viscosity modifiers may be needed, or preferred, for ensuring stability under extreme conditions when particular softener active levels are used. The surfactant concentration aids are typically selected from the group consisting of (1) single long chain alkyl cationic surfactants; (2) nonionic surfactants; (3) amine oxides; (4) fatty acids; and (5) mixtures thereof. These aids are described in WO 94/20597, specifically on page 14, line 12 to page 20, line 12, which is herein incorporated by reference.

When said dispersibility aids are present, the total level is from 0.1% to 20%, preferably from 0.2% to 10%, more preferably from 0.5% to 5%, and even more preferably from 1% to 2% by weight of the composition. These materials can either be added as part of the active softener raw material, (I), e.g., the mono-long chain alkyl cationic surfactant and/or the fatty acid which are reactants used to form the biodegradable fabric softener active as discussed hereinbefore, or added as a separate component. The total level of dispersibility aid includes any amount that may be present as part of component (I).

[0108] Inorganic viscosity/dispersibility control agents which can also act like or augment the effect of the surfactant concentration aids, include water-soluble, ionizable salts which can also optionally be incorporated into the compositions of the present invention. A wide variety of ionizable salts can be used. Examples of suitable salts are the halides of the Group IA and IIA metals of the Periodic Table of the Elements, e.g., calcium chloride, magnesium chloride, sodium chloride, potassium bromide, and lithium chloride. The ionizable salts are particularly useful during the process of mixing the ingredients to make the compositions herein, and later to obtain the desired viscosity. The amount of ionizable salts used depends on the amount of active ingredients used in the compositions and can be adjusted according to the desires of the formulator. Typical levels of salts used to control the composition viscosity are from about 20 to about 20,000 parts per million (ppm), preferably from about 20 to about 11,000 ppm, by weight of the composition. Alkylene polyammonium salts can be incorporated into the composition to give viscosity control in addition to or in place of the water-soluble, ionizable salts above. In addition, these agents can act as scavengers, forming ion pairs with anionic detergent carried over from the main wash, in the rinse, and on the fabrics, and may improve softness performance. These agents may stabilize the viscosity over a broader range of temperature, especially at low temperatures, compared to the inorganic electrolytes. Specific examples of alkylene polyammonium salts include L-lysine monohydrochloride and 1,5-diammonium 2-methyl pentane dihydrochloride.

(4) Stabilizers

[0109] Stabilizers can be present in the compositions of the present invention. The term "stabilizer," as used herein, includes antioxidants and reductive agents. These agents are present at a level of from 0% to about 2%, preferably from about 0.01% to about 0.2%, more preferably from about 0.035% to about 0.1% for antioxidants, and more preferably from about 0.01% to about 0.2% for reductive agents. These assure good odor stability under long term storage conditions for the compositions and compounds stored in molten form. The use of antioxidants and reductive agent stabilizers is especially critical for low scent products (low perfume).

[0110] Examples of antioxidants that can be added to the compositions of this invention include a mixture of ascorbic acid, ascorbic palmitate, propyl gallate, available from Eastman Chemical Products, Inc., under the trade names Tenox® PG and Tenox S-1; a mixture of BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), propyl gallate, and citric acid, available from Eastman Chemical Products, Inc., under the trade name Tenox-6; butylated hydroxytoluene, available from UOP Process Division under the trade name Sustane® BHT; tertiary butylhydroquinone, Eastman Chemical Products, Inc., as Tenox TBHQ; natural tocopherols, Eastman Chemical Products, Inc., as Tenox GT-1/GT-2; and butylated hydroxyanisole, Eastman Chemical Products, Inc., as BHA; long chain esters (C₆-C₂₂) of gallic acid, e.g., dodecyl gallate; Irganox® 1010; Irganox® 1035; Irganox® B 1171; Irganox® 1425; Irganox® 3114; Irganox® 3125; and mixtures thereof; preferably Irganox® 3125, Irganox® 1425, Irganox® 3114, and mixtures thereof; more preferably Irganox® 3125 alone. The chemical names and CAS numbers for some of the above stabilizers are listed in Table II below.

TABLE II

Antioxidant	CAS No.	Chemical Name used in Code of Federal Regulations
5 Irganox® 1010	6683-19-8	Tetrakis (methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)) methane
Irganox® 1035	41484-35-9	Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate
Irganox® 1098	23128-74-7	N,N'-Hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide
10 Irganox® B 1171	31570-04-4 23128-74-7	1:1 Blend of Irganox® 1098 and Irgafos® 168
Irganox® 1425	65140-91-2	Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl) phosphonate)
Irganox® 3114	65140-91-2	Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate)
15 Irganox® 3125 acid	34137-09-2	3,5-Di-tert-butyl-4-hydroxy-hydrocinnamic
Irgafos® 168	31570-04-4	triester with 1,3,5-tris(2-hydroxyethyl)-S-triazine-2,4,6-(1H, 3H, 5H)-trione Tris(2,4-di-tert-butyl-phenyl)phosphite

[0111] Examples of reductive agents include sodium borohydride, hypophosphorous acid, Irgafos® 168, and mixtures thereof.

5- PRESERVATIVE

[0112] Optionally, but preferably, antimicrobial preservative can be added to the composition of the present invention. Contamination by certain microorganisms with subsequent microbial growth can result in an unsightly and/or malodorous solution. Because microbial growth in solutions is highly objectionable when it occurs, it is highly preferable to include an antimicrobial preservative, which is effective for inhibiting and/or regulating microbial growth in order to increase storage stability of the composition.

[0113] It is preferable to use a broad spectrum preservative, e.g., one that is effective on both bacteria (both gram positive and gram negative) and fungi. A limited spectrum preservative, e.g., one that is only effective on a single group of microorganisms, e.g., fungi, can be used in combination with a broad spectrum preservative or other limited spectrum preservatives with complimentary and/or supplementary activity. A mixture of broad spectrum preservatives can also be used. In some cases where a specific group of microbial contaminants is problematic (such as Gram negatives), aminocarboxylate chelators, such as those described hereinbefore, can be used alone or as potentiators in conjunction with other preservatives. These chelators which include, e.g., ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, and other aminocarboxylate chelators, and mixtures thereof, and their salts, and mixtures thereof, can increase preservative effectiveness against Gram-negative bacteria, especially *Pseudomonas* species.

[0114] Antimicrobial preservatives useful in the present invention include biocidal compounds, i.e., substances that kill microorganisms, or biostatic compounds, i.e., substances that inhibit and/or regulate the growth of microorganisms. Well known preservatives such as short chain alkyl esters of p-hydroxybenzoic acid, commonly known as parabens; N-(4-chlorophenyl)-N'-(3,4-dichlorophenyl) urea, also known as 3,4,4'-trichlorocarbanilide or triclocarban; 2,4,4'-trichloro-2'-hydroxy diphenyl ether, commonly known as triclosan are useful preservative in the present invention.

[0115] Still other preferred preservatives are the water-soluble preservatives, i.e. those that have a solubility in water of at least about 0.3 g per 100 ml of water, i.e., greater than about 0.3% at room temperature, preferably greater than about 0.5% at room temperature.

[0116] The preservative in the present invention is included at an effective amount. The term "effective amount" as herein defined means a level sufficient to prevent spoilage, or prevent growth of inadvertently added microorganisms, for a specific period of time. In other words, the preservative is not being used to kill microorganisms on the surface onto which the composition is deposited in order to eliminate odors produced by microorganisms. Instead, it is preferably being used to prevent spoilage of the solution in order to increase the shelf-life of the composition. Preferred levels of preservative are from about 0.0001% to about 0.5%, more preferably from about 0.0002% to about 0.2%, most preferably from about 0.0003% to about 0.1%, by weight of the usage composition.

[0117] The preservative can be any organic preservative material which will not cause damage to fabric appearance, e.g., discoloration, coloration, bleaching. Preferred water-soluble preservatives include organic sulfur compounds, halogenated compounds, cyclic organic nitrogen compounds, low molecular weight aldehydes, quaternary ammonium compounds, dehydroacetic acid, phenyl and phenolic compounds, and mixtures thereof. Non-limiting examples of

preferred water-soluble preservatives for use in the present invention can be found in U.S. Patent 5,714,137, incorporated hereinbefore by reference, as well as co-pending application PCT/US 98/12154 pages 29 to 36.

[0118] Preferred water-soluble preservatives for use in the present invention are organic sulfur compounds. Some non-limiting examples of organic sulfur compounds suitable for use in the present invention are:

(a) 3-Isothiazolone Compounds

[0119] A preferred preservative is an antimicrobial, organic preservative containing 3-isothiazolone groups. This class of compounds is disclosed in U.S. Pat. No. 4,265,899, Lewis et al., issued May 5, 1981, and incorporated herein by reference. A preferred preservative is a water-soluble mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one, more preferably a mixture of about 77% 5-chloro-2-methyl-4-isothiazolin-3-one and about 23% 2-methyl-4-isothiazolin-3-one, a broad spectrum preservative available as a 1.5% aqueous solution under the trade name Kathon® CG by Rohm and Haas Company.

[0120] When Kathon® is used as the preservative in the present invention it is present at a level of from about 0.0001% to about 0.01%, preferably from about 0.0002% to about 0.005%, more preferably from about 0.0003% to about 0.003%, most preferably from about 0.0004% to about 0.002%, by weight of the composition.

[0121] Other isothiazolins include 1,2-benzisothiazolin-3-one, available under the trade name Proxel® products; and 2-methyl-4,5-trimethylene-4-isothiazolin-3-one, available under the trade name Promexal®. Both Proxel® and Promexal® are available from Zeneca. They have stability over a wide pH range (i.e., 4-12). Neither contain active halogen and are not formaldehyde releasing preservatives. Both Proxel® and Promexal® are effective against typical Gram negative and positive bacteria, fungi and yeasts when used at a level from about 0.001% to about 0.5%, preferably from about 0.005% to about 0.05%, and most preferably from about 0.01% to about 0.02% by weight of the usage composition.

(b) Sodium Pyrrithione

[0122] Another preferred organic sulfur preservative is sodium pyrrithione, with water solubility of about 50%. When sodium pyrrithione is used as the preservative in the present invention it is typically present at a level of from about 0.0001% to about 0.01%, preferably from about 0.0002% to about 0.005%, more preferably from about 0.0003% to about 0.003%, by weight of the usage composition.

[0123] Mixtures of the preferred organic sulfur compounds can also be used as the preservative in the present invention.

6- Antimicrobial active

[0124] The composition may suitably use an optional solubilized, water-soluble antimicrobial active, useful in providing protection against organisms that become attached to the treated material. The free, uncomplexed antimicrobial, e.g., antibacterial, active provides an optimum antibacterial performance.

[0125] Sanitization of fabrics can be achieved by the compositions of the present invention containing, antimicrobial materials, e.g., antibacterial halogenated compounds, quaternary compounds, and phenolic compounds.

[0126] Biguanides. Some of the more robust antimicrobial halogenated compounds which can function as disinfectants/sanitizers as well as finish product preservatives (vide infra), and are useful in the compositions of the present invention include 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with hydrochloric, acetic and gluconic acids. The digluconate salt is highly water-soluble, about 70% in water, and the diacetate salt has a solubility of about 1.8% in water. When chlorhexidine is used as a sanitizer in the present invention it is typically present at a level of from about 0.001% to about 0.4%, preferably from about 0.002% to about 0.3%, and more preferably from about 0.01% to about 0.1%, by weight of the usage composition. In some cases, a level of from about 1% to about 2% may be needed for virucidal activity.

[0127] Other useful biguanide compounds include Cosmocil® CQ®, Vantocil® IB, including poly (hexamethylene biguanide) hydrochloride. Other useful cationic antimicrobial agents include the bis-biguanide alkanes. Usable water soluble salts of the above are chlorides, bromides, sulfates, alkyl sulfonates such as methyl sulfonate and ethyl sulfonate, phenylsulfonates such as p-methylphenyl sulfonates, nitrates, acetates, gluconates, and the like.

[0128] As stated hereinbefore, the bis biguanide of choice is chlorhexidine and its salts, e.g., digluconate, dihydrochloride, diacetate, and mixtures thereof.

[0129] Quaternary Compounds. A wide range of quaternary compounds can also be used as antimicrobial actives, in conjunction with the preferred surfactants, for compositions of the present invention that do not contain cyclodextrin. Non-limiting examples of useful quaternary compounds include: (1) benzalkonium chlorides and/or substituted benzalkonium chlorides such as commercially available Barquat® (available from Lonza), Maquat® (available from Mason), Variquat® (available from Witco/Sherelex), and Hyamine® (available from Lonza); (2) dialkyl quaternary such as Bardac®

products of Lonza, (3) N-(3-chloroallyl) hexaminium chlorides such as Dowicide® and Dowicil® available from Dow; (4) benzethonium chloride such as Hyamine® 1622 from Rohm & Haas; (5) methylbenzethonium chloride represented by Hyamine® 10X supplied by Rohm & Haas; (6) cetylpyridinium chloride such as Cepacol chloride available from Merrell Labs. Typical concentrations for biocidal effectiveness of these quaternary compounds range from about 0.001% to about 0.8%, preferably from about 0.005% to about 0.3%, more preferably from about 0.01% to 0.2%, by weight of the usage composition. The corresponding concentrations for the concentrated compositions are from about 0.003% to about 2%, preferably from about 0.006% to about 1.2%, and more preferably from about 0.1 % to about 0.8% by weight of the concentrated compositions.

[0130] Other preservatives which are conventional in the art, such as described in US 5,593, 670 incorporated herein by reference, may also be used herein.

7-Perfume

[0131] The present invention can contain a perfume. Suitable perfumes are disclosed in U.S. Pat. 5,500,138, said patent being incorporated herein by reference.

[0132] As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such as fixatives, extenders, stabilizers and solvents. These auxiliaries are also included within the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds.

[0133] Examples of perfume ingredients useful in the perfumes of the present invention compositions include, but are not limited to, hexyl cinnamic aldehyde; amyl cinnamic aldehyde; amyl salicylate; hexyl salicylate; terpineol; 3,7-dimethyl-*cis*-2,6-octadien-1-ol; 2,6-dimethyl-2-octanol; 2,6-dimethyl-7-octen-2-ol; 3,7-dimethyl-3-octanol; 3,7-dimethyl-*trans*-2,6-octadien-1-ol; 3,7-dimethyl-6-octen-1-ol; 3,7-dimethyl-1-octanol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; tricyclodecyl propionate; tricyclodecyl acetate; anisaldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; ethyl-3-methyl-3-phenyl glycidate; 4-(para-hydroxyphenyl)-butan-2-one; 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; para-methoxyacetophenone; para-methoxy- α -phenylpropene; methyl-2-n-hexyl-3-oxo-cyclopentane carboxylate; undecalactone gamma.

[0134] Additional examples of fragrance materials include, but are not limited to, orange oil; lemon oil; grapefruit oil; bergamot oil; clove oil; dodecalactone gamma; methyl-2-(2-pentyl-3-oxo-cyclopentyl) acetate; beta-naphthol methyl ether; methyl-beta-naphthylketone; coumarin; decylaldehyde; benzaldehyde; 4-tert-butylcyclohexyl acetate; alpha, alpha-dimethylphenethyl acetate; methylphenylcarbonyl acetate; Schiff's base of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate; cyclic ethyleneglycol diester of tridecanedioic acid; 3,7-dimethyl-2,6-octadiene-1-nitrile; ionone gamma methyl; ionone alpha; ionone beta; petitgrain; methyl cedrylone; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene; ionone methyl; methyl-1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; benzophenone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-ol; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecan; cyclopentadecanone; 16-hydroxy-9-hexadecanoic acid lactone; 1,3,4,8,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; ambroxane; dodecahydro-3a,6,6,9a-tetramethylinaphtho-[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-eryl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; cedryl acetate; para-tert-butylcyclohexyl acetate; patchouli; oilbanum resinoid; labdanum; vetiver; copaiba balsam; fir balsam; and condensation products of: hydroxycitronellal and methyl anthranilate; hydroxycitronellal and indol; phenyl acetaldehyde and indol; 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate. More examples of perfume components are geraniol; geranyl acetate; linalool; linalyl acetate; tetrahydrolinalool; citronellol; citronellyl acetate; dihydromyrcenol; dihydromyrcenyl acetate; tetrahydromyrcenol; terpinyl acetate; nopil; nopyl acetate; 2-phenylethanol; 2-phenylethyl acetate; benzyl alcohol; benzyl acetate; benzyl salicylate; benzyl benzoate; styrallyl acetate; dimethylbenzylcarbinol; trichloromethylphenylcarbonyl methylphenylcarbonyl acetate; isononyl acetate; vetiveryl acetate; vetiverol; 2-methyl-3-(p-tert-butylphenyl)-propanal; 2-methyl-3-(p-isopropylphenyl)-propanal; 3-(p-tert-butylphenyl)-propanal; 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde; 4-acetoxy-3-pentyltetrahydropyran; methyl dihydrojasmonate; 2-n-heptylcyclopentanone; 3-methyl-2-pentyl-cyclopentanone; n-decanal; n-dodecanal; 9-decanol-1; phenoxyethyl isobutyrate; phenylacetaldehyde dimethylacetal; phenylacetaldehyde diethyl acetate; geranonitrile; citronellonitrile; cedryl acetal; 3-isocamphylcyclohexanol; cedryl methyl ether; isologilolanone; aubepine nitrile; aubepine; heliotropine; eugenol; vanillin; diphenyl oxide; hydroxycitronellal ionones; methyl ionones; isomethyl ionones; ionones; cis-3-hexenol and esters thereof; indane musk fragrances; tetralin musk fragrances; isochroman musk fragrances; macrocyclic ketones; macro lactone musk fragrances; ethylene brassylate.

[0135] The perfumes useful in the present invention compositions are substantially free of halogenated materials and nitromusks.

[0136] Suitable solvents, diluents or carriers for perfumes ingredients mentioned above are for examples, ethanol, isopropanol, diethylene glycol, monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, etc. The amount of such solvents, diluents or carriers incorporated in the perfumes is preferably kept to the minimum needed to provide a homogeneous perfume solution.

[0137] Perfume can be present at a level of from 0% to 10%, preferably from 0.1% to 5%, and more preferably from 0.2% to 3%, by weight of the finished composition. Fabric softener compositions of the present invention provide improved fabric perfume deposition.

[0138] Perfume ingredients may also be suitably added as releasable fragrances, for example, as pro-perfumes or pro-fragrances as described in U.S. 5,852,205 Hartman et al., issued July 29, 1997, WO95/04809, WO96/02625, PCT US97/14610 filed 19 August 1997 and claiming priority of 19 August 1996, EP-A-0,752,465, co-pending application EP 98870227.0, EP 98870226.2, EP 99870026.4, and EP 99870025.6; all incorporated herein by reference.

8- Soil Release Agent

[0139] Soil Release agents are desirably used in compositions of the instant invention. Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

[0140] If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

[0141] The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 3,959,230 Hays, issued May 25, 1976; U.S. 3,893,929 Basador, issued July 8, 1975; U.S. 4,000,093, Nicol, et al., issued December 28, 1976; U.S. Patent 4,702,857 Gosselink, issued October 27, 1987; U.S. 4,968,451, Scheibel et al., issued November 6, U.S. 4,702,857, Gosselink, issued October 27, 1987; U.S. 4,711,730, Gosselink et al., issued December 8, 1987; U.S. 4,721,580, Gosselink, issued January 26, 1988; U.S. 4,877,896, Maldonado et al., issued October 31, 1989; U.S. 4,958,447, Gosselink et al., issued September 11, 1990; U.S. 5,415,807 Gosselink et al., issued May 16, 1995; European Patent Application 0 219 048, published April 22, 1987 by Kud, et al.

[0142] Further suitable soil release agents are described in U.S. 4,201,824, Violland et al.; U.S. 4,240,918 Lagasse et al.; U.S. 4,525,524 Tung et al.; U.S. 4,579,681, Ruppert et al.; U.S. 4,240,918; U.S. 4,787,989; U.S. 4,525,524; EP 279,134 A, 1988, to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N. V., 1974 all incorporated herein by reference.

[0143] Commercially available soil release agents include the METOLOSE SM100, METOLOSE SM200 manufactured by Shin-etsu Kagaku Kogyo K.K.; SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (Germany), ZELCON 5126 (from Dupont) and MILEASE T (from ICI).

9-pH

[0144] An optional requirement of the compositions according to the present invention is that the pH as measured in the neat compositions at 20 °C, is greater than 3, preferably between 3 and 12, more preferably between 4 and 8, most preferably is of 5. This range is preferred for fabric safety. The pH of these compositions herein can be regulated by the addition of a Bronsted acid.

10- Other Optional Ingredients

[0145] The present invention can include optional components conventionally used in textile treatment compositions, for example, humectants like diethylene glycol, and/or salts like lithium salts, colorants, bactericides, optical brighteners, opacifiers, anti-shrinkage agents, germicides, fungicides, anti-oxidants, color protection agent like dye fixing agent as described in EP 93/133, enzymes, chelating agents, cyclodextrin as described in WO 98/56888, metallic salts to absorb amine and sulfur-containing compounds and selected from the group consisting of copper salts, zinc salts, and mixtures thereof, water-soluble polyionic polymers, e.g., water-soluble cationic polymer like polyamines, and water-soluble anionic polymers like polyacrylic acids, other antistatic agent, insect and/or moth repelling agents, colorants and dyes, anti-clogging agent, and the like; typical disclosure of which can be found in WO 98/56888. Still other suitable optional ingredients are ingredients which provide shield protection against stain like hydroxypropylcellulose as well as other

cellulosic polymer like carboxymethylcellulose. The compositions are preferably free of any material that would soil or stain fabric, and are also substantially free of starch. Typically, there should be less than about 0.5%, by weight of the composition, preferably less than about 0.3%, more preferably less than about 0.1%, by weight of the composition, of starch and/or modified starch.

Form of the composition

[0146] The composition of the invention may take a variety of physical form including liquid, liquid-gel, paste-like, foam in either aqueous or non-aqueous form, powder like granular and tablet forms. A preferred form of the composition is in a liquid form.

[0147] When in a liquid form, the composition is preferably dispensed by a dispensing means such as a spray dispenser, aerosol dispenser, or refill thereof. Still another preferred dispensing means is by incorporation of the composition of the invention in the ironing tank per se, or via a cartridge preferably adapted for the iron.

Spray Dispenser

[0148] The present invention also relates to such compositions incorporated into a spray dispenser to create an article of manufacture that can facilitate treatment of fabric articles and/or surfaces with the compositions according to the invention at a level that is effective. The spray dispenser comprises manually activated and non-manual powered (operated) spray means and a container containing the treating composition. Typical disclosure of such spray dispenser can be found in WO 96/04940 page 19 line 21 to page 22 line 27. Preferably, the spray dispenser is selected from spray dispenser comprising battery operated pump, spray dispenser comprising a trigger spray device, spray dispenser comprising a pressurized aerosol spray dispenser.

Method of use

[0149] It has been found that the use of the water-soluble lubricant provided a reduction of the WRA compared to water. Accordingly, there is provided a method of increasing the WRA of fabrics, which comprises the steps of contacting the fabrics with a water-soluble lubricant as defined herein before, using a domestic process.

[0150] It has also been found that the use of the water-soluble lubricant or composition of the invention provides surprisingly good benefit on the dewrinkling performance upon wearing. This benefit is particularly achieved while spraying the compound or composition from the iron. Accordingly, there is also provided a method of treating fabrics, in particular to provide in wear wrinkle resistance on fabrics, which comprises the steps of contacting the fabrics with a water-soluble lubricant or composition according to the invention, as defined herein before, using a domestic process.

[0151] By "contacting", it is meant any steps that is suitable for providing a contact of the composition with the fabric. This can include by soaking, washing, rinsing, and/or spraying as well as by means of a dryer sheet onto which is adsorbed the composition. Preferably, the contacting occurs after the laundering and optional drying of the fabrics, e. g. by spraying, more preferably by spraying from the iron spray dispenser and/or via the vaporisation holes from the iron sole. Accordingly, in this instance, the composition of the present invention is used as an ironing aid. An effective amount of the composition can be sprayed onto fabric, wherein said fabric should not be sprayed to saturation. Still another preferred way of treating the fabrics is when the fabric can be sprayed with an effective amount of the composition, allowed to dry and then ironed, or sprayed and ironed immediately.

[0152] Accordingly, in a further aspect of the invention, the composition of the invention can also be sprayed onto the fabrics by means of an iron spraying means, whereby the composition is incorporated into the iron as is or via a cartridge, preferably adapted for the iron. As for the method of spraying via the iron, the spraying means should preferably be capable of providing droplets with a weight average diameter of from about 40 to about 200 μm , preferably from about 70 to about 150 μm . Preferably, the loading of moisture on fabrics made of natural and synthetic fibers is from about 5 to about 25%, more preferably from about 5 to about 10% by weight of the dried fabric.

[0153] By "wrinkle reducing composition", it is meant that the composition is tested on 100% cotton, woven Oxford pinpoint fabric according to the procedure given in W. Garner, Textile Laboratory Manual Vol. 6, Ed. 3, Elsevier Inc., 1967, p. 105, so called "cylinder test". The cylinder test consists in taking a 12X14 inch of treated cloth, rolling it round a plastic tube, placing the roll in a 360 ml measuring cylinder (= 0.67 inch, i.e. 15.7 inch), withdrawing the tube, and pushing the fabric down to occupy a volume of about 90 ml by means of a plastic tube which is an easy sliding fit for the cylinder. This test is carried out on cloth conditioned for 24 hours at 21°C (70°F) and 65% RH. The cloth is left 1 minute in the cylinder, opened immediately, inspected visually, and then compared with a cloth only treated with water. The results obtained are compared against fabrics which have only been treated with water. Wrinkle reducing compositions are compositions which provide a better crease resistance versus water, i.e. fabrics that have been treated with a composition of the invention show less wrinkles compared to fabrics which have only been treated with water.

[0154] In a still further aspect of the invention, the composition can be sprayed onto fabrics by an in-home de-wrinkling chamber containing the fabric to be dewrinkled, thereby providing ease of operation. Conventional personal as well as industrial de-wrinkling apparatuses are suitable for use herein. Traditionally, these apparatuses act by a steaming process which effects a relaxation of the fibers. Examples of home dewrinkling chambers include shower stalls. The spraying of the composition or compounds onto the fabrics can then occur within the chamber of the apparatus or before placing the fabrics into the chamber. As for the manual method of spraying, the spraying means should preferably be capable of providing droplets with a weight average diameter of from about 8 to about 100 μm , preferably from about 10 to about 50 μm . Preferably, the loading of moisture on fabrics made of natural and synthetic fibers is from about 5 to about 25%, more preferably from about 5 to about 10% by weight of the dried fabric. Other conventional steps that can be carried out in the dewrinkling apparatus can be applied such as heating which will provide the curing step and drying. Preferably, for optimum dewrinkling benefit, the temperature profile inside the chamber ranges from about 40°C to about 80°C, more preferably from about 50°C to about 70°C. The preferred length of the drying cycle is from about 15 to about 60 minutes, more preferably from about 20 to about 45 minutes.

[0155] The steaming step in the dewrinkling apparatus can also be eliminated if the composition is maintained at a temperature range from about 22°C (about 72° F) to about 76°C (170° F) before spraying.

[0156] The present invention encompasses the method of spraying a mist of an effective amount of solution of the invention composition onto fabric and/or fabric articles. Preferably, said fabric and/or fabric articles include, but are not limited to, clothes, curtains, drapes, upholstered furniture, carpeting, bed linens, bath linens, tablecloths, sleeping bags, tents, car interiors, etc.

[0157] The compositions herein are especially useful, when used to treat garments for extending the time before another wash cycle is needed, and/or even reducing the time involved in ironing. Such garments include uniforms and other garments which are normally treated in an industrial process, which can be dewrinkled and the time between treatments extended.

[0158] Also provided herein is an article of manufacture comprising a container and the composition of the invention in association with a set of instructions to use the composition in an amount effective to provide a solution to problems involving and/or provision of a benefit related to those selected from reducing wrinkles; imparting in-wear resistance to fabrics. It is important that the consumer be aware of these additional benefits, since otherwise the consumer would not know that the composition would solve these problems and/or provide these benefits.

[0159] As used herein, the phrase "in association with" means the set of instructions are either directly printed on the container itself or presented in a separate manner including, but not limited to, a brochure, print advertisement, electronic advertisement, and/or verbal communication, so as to communicate the set of instructions to a consumer of the article of manufacture. The set of instructions preferably comprises the instruction to apply an effective amount of the composition, preferably by spraying, to provide the indicated benefit, e.g., wrinkles reduction; imparting in-wear resistance to fabrics.

[0160] The invention is illustrated in the following non limiting examples, in which all percentages are on a weight basis unless otherwise stated.

[0161] In the examples, the abbreviated component identifications have the following meanings:

Polymer 1: Isomaltol oligosaccharide available from Showa Sangyo Co. under the trade name IMO 900

Polymer 2: Polyvinylpyrrolidone available from BASF under the trade name Luviskol K30

Polymer 3: Co-polymer of vinylpyrrolidone and vinylcaprolactame available from BASF under the trade name Luvitec VPC

Polymer 4: Co-polymer of vinylpyrrolidone and vinylimidazolium methachloride available from BASF under the trade name Luviquat FC 905

Lubricant 1: Polyalkylene oxide polysiloxane commercially available under the tradename of Silwet 7200 from OSI Chem./Witco

Lubricant 2: Polyalkylene oxide polysiloxane commercially available under the tradename of Silwet 7657 from OSI Chem./Witco

Lubricant 3: Polyethoxylated (20 moles) sorbitan monolaurate commercially available under the tradename of Radasurf 7137 from FINA

Lubricant 4: Polyethoxylated (20 moles) sorbitan tristearate commercially available under the tradename of Tween

65

Wetting agent 1: Polyalkylene oxide polysiloxane commercially available under the tradename of Silwet 7600 from OSI Chem./Witco

Wetting agent 1: Polyalkylene oxide polysiloxane commercially available under the tradename of Silwet L 77 from OSI Chem./Witco

Emulsifier 1: CAE 10 (coconut alcohol condensed with an average of 10 moles of ethylene oxide)

	A	B	C	D	E	F
Polymer #1	5%	-	-	-	-	1%
Polymer #2	-	1%	-	2%	-	-
Polymer #3	-	-	2%	-	-	-
Polymer #4	-	-	-	-	0.5 %	-
Lubricant #1	14%	4%	-	-	1.5%	-
Lubricant #2	-	-	6%	2%	1.5%	-
Lubricant #3	8 %	2 %	-	-	-	5%
Lubricant #4	-	-	-	3 %	-	-
Wetting agent 1	3 %	0.5	-	-	0.2 %	-
Wetting agent 2	-	-	0.5 %	-	-	-
Dipropylene glycol	-	0.3	-	-	-	-
Emulsifier 1	0.6 %	0.2	-	-	-	-
Cyclodextrin	-	0.5	1 %	-	-	-
Preservative	3 ppm	3 ppm	-	3 ppm	-	-
Perfume	0.5 %	0.1	0.1 % -	-	-	0.2%
Water	Balance	Balance	Balance	Balance	Balance	Balance

Claims

1. A fabric wrinkle reducing composition comprising a water-soluble lubricant and a component having a deviation of fabric Wrinkle Recovery angle (WRA) versus water of at least +15.
2. A composition according to Claim 1, wherein the water-soluble lubricant is selected from nonionic silicone containing surfactants, sorbitan esters, ethoxylated sorbitan esters, and mixtures thereof.
3. A composition according to either one of Claims 1 or 2, wherein the water-soluble lubricant is present in an amount of from 0.1% to 70% by weight of the composition.
4. A composition according to any one of Claims 1-3, wherein the component having a deviation of fabric WRA versus water of at least +15 is a polymer, preferably selected from shape retention polymers, polymers comprising at least one unit which provide a dye transfer inhibiting benefit, urethane polymers, isomaltoligosaccharide, polyvinylamine polymers, and mixtures thereof.
5. A composition according to any one of Claims 1-4, wherein the component having a deviation of fabric WRA versus water of at least +15 is present in an amount of at least about 0.01%, preferably from about 0.1% to about 20%, preferably to about 10% by weight of the composition.
6. A composition according to any one of Claims 1-5, wherein the water-soluble lubricant and the component having a deviation of fabric WRA versus water of at least +15 are present in a weight ratio of from 10:1 to 1:1.
7. A composition according to any one of Claims 1-6, wherein the composition is a liquid composition, preferably a liquid aqueous composition.

8. An article of manufacture comprising a composition according to any of Claims 1-7, wherein preferably the article is selected from an aerosol, a spray dispenser, a refill, a cartridge, an iron, and a foam dispenser.
9. The article of manufacture of Claim 8 wherein said article is a spray dispenser selected from spray dispenser comprising battery operated pump, spray dispenser comprising a trigger spray device, spray dispenser comprising a pressurized aerosol spray dispenser, spray dispenser comprising a non-manually operated spray dispenser.
10. A method for treating the fabrics which comprises the steps of contacting the fabric with a water-soluble lubricant or composition according to any one of Claims 1-9, preferably subsequently cure the fabric.
11. A method according to Claim 10, wherein said method provides a reduction of the time and/or effort involved to iron fabrics.
12. A method according to either one of Claim 10 or 11, wherein said method increases the fabric WRA.
13. A method according to either one of Claim 10-12, wherein said method provides in-wear resistance to treated fabrics.
14. A method according to any one of Claims 9-13, wherein said method is performed in an in-home dewrinkling apparatus.
15. A method according to any one of Claims 9-13, wherein said method is performed with an iron.
16. An article of manufacture comprising a container and the composition of any one of Claims 1-7 in association with instructions to use an effective amount of said composition on fabric to provide at least one benefit selected from the group consisting of: reducing wrinkles; reducing the time and/or effort involved to iron fabrics, imparting in-wear resistance to fabrics.
17. Use of a composition as defined in any one of Claims 1-7, or cartridge as defined in Claim 8, in an iron for treating fabrics.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 87 0223

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 4 376 802 A (MARSHALL ROBERT M) 15 March 1983 (1983-03-15) * claims *	1, 3, 4, 7	D06M23/06
X	GB 827 647 A (TOOTAL BROADHURST LEE CO LTD) * page 1, line 14 - page 3, line 33; claims *	1, 3, 4, 7	
X	GB 674 948 A (MONSANTO CHEMICAL CO) * page 2, line 37 - page 3, line 35; claims *	1, 4, 7, 8	
A	US 5 100 566 A (LANE THOMAS H ET AL) 31 March 1992 (1992-03-31) * claims *	1, 2, 7, 8	
A	US 4 661 268 A (JACOBSON JEFF A ET AL) 28 April 1987 (1987-04-28) * claims *	1, 2, 7, 8	
A	US 5 573 695 A (TARGOSZ EUGENE F) 12 November 1996 (1996-11-12) * column 3, line 25 - column 8, line 22; claims *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7) D06M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31 May 2000	Examiner Hellemans, W
CATEGORY OF CITED DOCUMENTS X particularly relevant if taken alone Y particularly relevant if combined with another document of the same category A technological background Q non-written disclosure I intermediate document T theory or principle underlying the invention E* earlier patent document, but published on, or after the filing date D document cited in the application L document cited for other reasons & member of the same patent family, corresponding document			

EP 1 096 060 A1 (2000/05/04)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 99 87 0223

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EPO file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

31-05-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4376802 A	15-03-1983	NONE	
GB 827647 A		BE 552145 A BE 552146 A FR 1163125 A FR 1163126 A GB 855509 A	22-09-1958 22-09-1958
GB 674948 A		NONE	
US 5100566 A	31-03-1992	CA 2060141 A JP 4316671 A	05-08-1992 09-11-1992
US 4661268 A	28-04-1987	AU 6671086 A BR 8606406 A CA 1258754 A DK 621386 A EP 0228261 A JP 62170580 A NO 865282 A PH 23309 A	25-06-1987 13-10-1987 29-08-1989 25-06-1987 08-07-1987 27-07-1987 25-06-1987 30-06-1989
US 5573695 A	12-11-1996	CA 2187468 A,C	20-06-1997

EPO FORM 1989

For more details about this annex "see Official Journal" of the European Patent Office, No. 12/82



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 3/37		A1	(11) International Publication Number: WO 97/42287
			(43) International Publication Date: 13 November 1997 (13.11.97)
(21) International Application Number: PCT/US97/06989		(72) Inventors: PRAMOD, Kakumanu; 7986 Kingfisher Lane, West Chester, OH 45069 (US). PANANDIKER, Rajan, Keshav; 6484 Oregon Pass, West Chester, OH 45069 (US). GHOSH, Chanchal, Kumar; 7005 Pinemill Drive, West Chester, OH 45069 (US). WATSON, Randall, Alan; 14 Penderly Avenue, Cincinnati, OH 45215 (US). KONG-CHAN, Josephine, Ling; 12106 Paulmeadows Drive, Cincinnati, OH 45249 (US). DE BUZZACCARINI, Francesco; 17A, rue Vilain XIII, B-1050 Brussels (BE).	
(22) International Filing Date: 25 April 1997 (25.04.97)		(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).	
(30) Priority Data:		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
60/016,525 3 May 1996 (03.05.96) US 60/016,527 3 May 1996 (03.05.96) US 60/017,062 3 May 1996 (03.05.96) US 60/017,059 3 May 1996 (03.05.96) US 60/017,050 3 May 1996 (03.05.96) US 60/016,526 3 May 1996 (03.05.96) US 60/016,531 3 May 1996 (03.05.96) US 60/016,528 3 May 1996 (03.05.96) US 60/027,902 3 May 1996 (03.05.96) US 60/027,899 3 May 1996 (03.05.96) US			
(71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(54) Title: LIQUID DETERGENT COMPOSITIONS COMPRISING SPECIALLY SELECTED MODIFIED POLYAMINE POLYMERS			
(57) Abstract			
Laundry detergent compositions that provide fabric appearance benefits to all fabric comprising modified polyamine agents and other selected fabric appearance agents, and a method for providing these benefits to fabric by contacting fabric articles with a water soluble and/or dispersible, modified polyamine having functionalized backbone moieties.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LJ	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

LIQUID DETERGENT COMPOSITIONS COMPRISING SPECIALLY SELECTED MODIFIED POLYAMINE POLYMERS

PRIOR HISTORY

This application claims priority to the following pending applications: U.S. Serial No. 60/016,527, filed May 3, 1996; U.S. Serial No. 60/017,062, filed May 3, 1996; U.S. Serial No. 60/016,525, filed May 3, 1996; U.S. Serial No. 60/017,059, filed May 3, 1996; U.S. Serial No. 60/017,060, filed May 3, 1996; U.S. Serial No. 60/016,526, filed May 3, 1996; U.S. Serial No. 60/016,531, filed May 3, 1996; U.S. Serial No. 60/016,528, filed May 3, 1996; U.S. Serial No. 60/027,902, filed October 7, 1996; and U.S. Serial No. 60/027,899, filed October 7, 1996.

FIELD OF THE INVENTION

The present invention relates to liquid laundry detergent compositions that provide fabric appearance benefits to fabric under a variety of soil conditions. The compositions herein comprise specially selected modified polyamine fabric appearance agents. The present invention also relates to a method for providing fabric appearance benefits to fabrics by contacting fabric articles with a water soluble and/or dispersible, modified polyamine.

BACKGROUND OF THE INVENTION

A wide variety of fabric appearance agents for use in domestic and industrial fabric treatment processes such as laundering, fabric drying in hot air clothes dryers, and the like are known in the art. Various fabric appearance agents, including soil release agents, dispersants, surfactants, fabric softeners, and dye transfer inhibitors, have been commercialized and are currently used in detergent compositions and fabric softener/antistatic articles and compositions.

Extensive research in this area has yielded significant improvements in the effectiveness of the various fabric appearance agents, providing enhanced product performance and formulatability. However, no one single compound has been identified which can perform a number of these fabric appearance enhancements. Thus, formulators must pick and choose among several technologies to achieve the overall performance expected by consumers in a cost effective manner. The problem is compounded in liquid detergents because of the potential interactions of the various agents in an aqueous solution.

Moreover, many of these conventional fabric appearance agents do not provide enhanced performance on both hydrophobic and hydrophilic soils and stains. Tea stains are hydrophilic. Dirt and tomato stains are hydrophobic.

Thus, until now the development of an effective, all-around fabric appearance agent for use in a laundry detergent has been elusive. Attempts by others to apply the paradigm of matching the structure of a polymer with the structure of the fabric, a method successful in the polyester soil release polymer field, has nevertheless yielded marginal results.

It has now been surprisingly discovered that effective fabric appearance agents can be prepared from certain modified polyamines. This unexpected result has yielded compositions that are key to the present method for providing several fabric appearance benefits, i.e., soil removal, dispersal of soils, and dye transfer inhibition, once available to only with the use of several individual laundry additives. The process or method of the present invention also provides benefits on all types of soils and stains.

The process or method of the present invention is especially effective when the laundry detergent compositions disclosed herein are liquid. The liquid detergents can have a wide range of viscosity and may include heavy concentrates, pourable "ready" detergents, or light duty fabric pre-treatments.

The modified polyamines disclosed in the present method are compatible with other laundry detergent additives and adjuncts. In fact, it is believed that the polyamines of this invention actually compliment and enhance the performance of other detergent additives, such as surfactants and additives that before now can cause negative dye transfer problems.

BACKGROUND ART

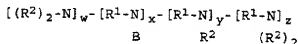
U.S. Patent 4,548,744, Connor, issued October 22, 1985; U.S. Patent 4,597,898, Vander Meer, issued July 1, 1986; U.S. Patent 4,877,896, Maldonado, et al., issued October 31, 1989; U.S. Patent 4,891,160, Vander Meer, issued January 2, 1990; U.S. Patent 4,976,879, Maldonado, et al., issued December 11, 1990; U.S. Patent 5,415,807, Gosselink, issued May 16, 1995; U.S. Patent 4,235,735, Marco, et al., issued November 25, 1980; WO 95/32272, published November 30, 1995; U.K. Patent 1,537,288, published December 29, 1978; U.K. Patent 1,498,520, published January 18, 1978; German Patent DE 28 29 022, issued January 10, 1980; Japanese Kokai JP 06313271, published April 27, 1994. See also U.K. 1,314,897; U. S. Patent No. 3,897,026; U.S. Patent No. 3,912,681; U.S. Patent No. 3,948,838 issued to Hinton, *et alia* describes high molecular weight (500,000 to 1,500,000) polyacrylic polymers for soil release; U.S. Patent 4,559,056; U.S. Patent No. 4,579,681; U.S. Patent No. 4,614,519.

Examples of alkoxylated polyamines and quaternized alkoxylated polyamines are disclosed in European Patent Application 206,513 as being suitable for use as soil dispersants, however their possible use as a cotton soil release agent is not disclosed.

SUMMARY OF THE INVENTION

Submitted herein are liquid laundry detergent compositions comprising:

- a) at least about 0.1% by weight, of a deterative surfactant selected from anionic surfactants, nonionic surfactants, or mixtures thereof;
- b) at least about 0.05% by weight, of a water-soluble or dispersible, modified polyamine agent, said agent comprising a polyamine backbone corresponding to the formula:



wherein each R^1 is independently C_2 - C_5 alkylene, alkenylene or arylene; each R^2 is independently H, or a moiety of formula $OH[(CH_2)_xO]_n$, wherein x is from about 1 to about 8 and n is from about 10 to about 50; w is 0 or 1; $x+y+z$ is from about 5 to about 30; and B represents a continuation of this structure by branching; and wherein said polyamine before alkylation has an average molecular weight of from about 300 to about 1,200; and

- c) one or more additional deterative additives selected from the group consisting of amylase, deterative amine, cationic surfactants, antiredeposition agents, antifading agent, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof.

The detergent compositions herein can comprise additional adjunct ingredients selected from the group consisting of builders, optical brighteners, soil release polymers, dye transfer inhibitors, polymeric dispersing agents, non-amylase enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, and mixtures thereof.

In preferred embodiments, R^1 is C_2 - C_4 alkylene, more preferably ethylene; R^2 is $OH[(CH_2CH_2O)]_n$, wherein n is from about 15 to about 30, more preferably n is about 20. The average Molecular Weight of the polyamine before alkylation is from about 300 to about 1200, more preferably from about 500 to about 900, still more preferably from about 600 to about 700, even more preferably from about 600 to about 650.

The present invention further relates to a method of providing dye transfer inhibiting and other fabric appearance benefits to fabric by contacting said fabric with a laundry composition comprising:

- a) at least about 0.05% by weight, of a water-soluble or dispersible, modified polyamine agent as disclose above; and
- b) one or more additional deterative additives selected from the group consisting of selected amylases, selected deterative amines, selected cationic surfactants,

antiredeposition agents, antifading agent, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof.

The detergent compositions of this invention may be in liquid, gel or structured liquid form.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius ($^{\circ}$ C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

Preferred laundry detergent compositions of this invention comprise:

- a) from about 0.1% to about 95% by weight, of an anionic deterative surfactant, preferably selected from alkyl sulfates, alkyl alkoxy (preferably ethoxy) sulfates, and mixtures thereof;
- b) at least about 0.1% to about 95% by weight, of a nonionic deterative surfactant, preferably selected from polyhydroxy fatty acid amides and alky ethoxylates;
- c) from about 0.05% to about 15% by weight, preferably from about 0.1% to about 10%, of a water-soluble or dispersible modified polyamine fabric appearance agent of this invention;
- d) one or more additional deterative additives selected from the group consisting of amylase, deterative amine, cationic surfactants, antiredeposition agents, antifading agent, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof; and
- e) the balance carrier and adjunct ingredients.

The compositions of this invention preferably have a pH of about 6 to about 12, more preferably from about 7.0 to about 10.5, when measured as a 10% solution in water.

Modified Polyamines -The present invention employs an "effective amount" of the polyamine fabric appearance agent herein to improve the performance of cleaning compositions which contain other adjunct ingredients. By an "effective amount" herein is meant an amount which is sufficient to improve, either directionally or significantly at the 90% confidence level, the performance of the cleaning composition against at least some of the target soils and stains. Thus, in a composition whose targets include certain food stains, the formulator will use sufficient polyamine fabric appearance agent to at least directionally improve cleaning performance against such stains. Importantly, in a fully-formulated laundry detergent the fabric appearance agents can be used at levels which provide at least a directional improvement in cleaning performance over a wide variety of soils and stains, as will be seen from the data presented hereinafter.

As noted, the fabric appearance agents are used herein in detergent compositions in combination with deterative surfactants at levels which are effective for achieving at least a directional improvement in cleaning performance. In the context of a fabric laundry composition, such "usage levels" can vary depending not only on the type and severity of the soils and stains, but also on the wash water temperature, the volume of wash water and the type of washing machine.

As can be seen from the foregoing, the amount of fabric appearance agent used in a machine-wash laundering context can vary, depending on the habits and practices of the user, the type of washing machine, and the like. In this context, however, one heretofore unappreciated advantage of the fabric appearance agents is their ability to provide at least directional improvements in performance over a spectrum of soils and stains.

The modified polyamine agents of the present invention are water-soluble or dispersible, modified polyamines. These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also comprise polyamine branching chains to a greater or lesser degree. In general, the polyamine backbones described herein are modified in such a manner that each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, or combinations thereof.

For the purposes of the present invention the term "modification" is defined as replacing a backbone -NH hydrogen atom by an E unit (substitution) or by quaternizing a backbone nitrogen (quaternized). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an E unit. Quaternization may take place in some circumstances without substitution.

Preferred polymers of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

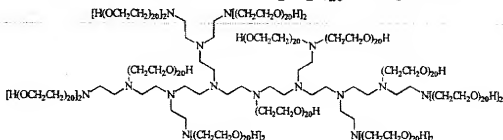
The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's), or PEA's or PEI's connected by moieties having longer R units than the parent PAA's, PAI's, PEA's or PEI's. A common polyalkyleneamine (PAA) is tetrabutylene-pentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional

distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

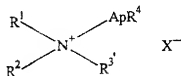
Preferred amine polymer backbones comprise R units that are C₂ alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of about 2:1 are most preferred.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

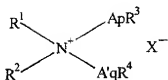
The following formula depicts a preferred modified polyamine agent comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $(-\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, having the formula:



Cationic Surfactants - The alkoxyated quaternary ammonium (AQA) surfactants useful in the present invention are of the general formula:



1



II

wherein R^1 is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms; R^2 and R^3 are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl; R^3 and R^4 can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is selected from C_1 - C_4 alkoxy, especially ethoxy (i.e.,

$-CH_2CH_2O-$), propoxy, butoxy and mixtures thereof; and for formula I, p is from 2 to about 30, preferably 2 to about 15, most preferably 2 to about 8; and for formula II, p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

The levels of the AQA surfactants used to prepare finished laundry detergent compositions can range from about 0.1% to about 5%, typically from about 0.45% to about 2.5%, by weight.

Amylase - Complete removal of the very hydrophobic "everyday" or "body" soils is difficult and low levels of residual soils often remain on the fabric after washing. These residues build up and act like an amorphous glue between the fibers, entrapping particulate dirt and leading to fabric yellowing. It has now further been discovered that detergent compositions containing a combination of the water-soluble polyamine agents herein and amylase enzymes delivers superior cleaning and whiteness performance vs. compositions containing either technology alone.

Such amylase enzymes include those described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056. These enzymes are incorporated into detergent compositions at a level from 0.00018% to 0.060% pure enzyme by weight of the total composition, more preferably from 0.00024% to 0.048% pure enzyme by weight of total weight composition.

Specific amylase enzymes for use in the detergent compositions of the present invention therefore include:

(a) α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value

in the range of 8 to 10, measured by the Phadebas[®] α -amylase activity assay. Such Phadebas[®] α -amylase activity assay is described at pages 9-10, WO95/26397.

(b) α -amylases according (a) comprising the amino sequence shown in the SEQ ID listings in the above cited reference, or an α -amylase being at least 80% homologous with the amino acid sequence shown in the SEQ ID listing.

(c) α -amylases according (a) comprising the following amino sequence in the N-terminal : His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp.

A polypeptide is considered to be X% homologous to the parent amylase if a comparison of the respective amino acid sequences, performed via algorithms, such as the one described by Lipman and Pearson in Science 227, 1985, p. 1435, reveals an identity of X%

(d) α -amylases according (a-c) wherein the α -amylase is obtainable from an alkalophilic Bacillus species; and in particular, from any of the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935.

In the context of the present invention, the term "obtainable from" is intended not only to indicate an amylase produced by a Bacillus strain but also an amylase encoded by a DNA sequence isolated from such a Bacillus strain and produced in a host organism transformed with said DNA sequence.

(e) α -amylase showing positive immunological cross-reactivity with antibodies raised against an α -amylase having an amino acid sequence corresponding respectively to those α -amylases in (a-d).

(f) Variants of the following parent α -amylases which (i) have one of the amino acid sequences shown in corresponding respectively to those α -amylases in (a-e), or (ii) displays at least 80% homology with one or more of said amino acid sequences, and/or displays immunological cross-reactivity with an antibody raised against an α -amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence which hybridizes with the same probe as a DNA sequence encoding an α -amylase having one of said amino acid sequence; in which variants :

1. at least one amino acid residue of said parent α -amylase has been deleted; and/or
2. at least one amino acid residue of said parent α -amylase has been replaced by a different amino acid residue; and/or
3. at least one amino acid residue has been inserted relative to said parent α -amylase; said variant having an α -amylase activity and exhibiting at least one of the following properties relative to said parent α -amylase : increased thermostability, increased stability towards oxidation, reduced Ca ion dependency, increased stability and/or α -

amylolytic activity at neutral to relatively high pH values, increased α -amylolytic activity at relatively high temperature and increase or decrease of the isoelectric point (pI) so as to better match the pI value for α -amylase variant to the pH of the medium.

The preferred amylases of this invention are those described by the following:

- (a) α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α -amylase activity assay;
- (b) α -amylase showing positive immunological cross-reactivity with antibodies raised against an α -amylase having an amino acid sequence corresponding respectively to those α -amylases in (a); and
- (c) mixtures thereof.

Said variants are described in the patent application PCT/DK96/00056.

Other amylases suitable herein include, for example, α -amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful.

Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp. 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents, especially improved oxidative stability as measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597.

Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* α -amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Such preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B. licheniformis* α -amylase, known as TERMAMYL®, or the homologous position

variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B. subtilis*, or *B. stearothermophilus*; (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B. licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Other Enzymes - enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from surfaces such as textiles or dishes, for the prevention of refugee dye transfer, for example in laundering, and for fabric restoration. Suitable other enzymes include proteases, lipases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases.

"Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent composition.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. In practical terms for current

commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may be desirable in highly concentrated detergent formulations.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Proteases - Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO

9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

In more detail, an especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al, entitled "Protease-Containing Cleaning Compositions" having US Serial No. 08/322,676, and C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, both filed October 13, 1994.

Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303,761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein, Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985.

Also preferred proteases are subtilisin enzymes, in particular BPN', that have been modified by mutating the various nucleotide sequences that code for the enzyme, thereby modifying the amino acid sequence of the enzyme. These modified subtilisin enzymes have decreased adsorption to and increased hydrolysis of an insoluble substrate as compared to the wild-type subtilisin. Also suitable are mutant genes encoding for such BPN' variants.

Preferred BPN' variants comprise wild-type amino acid sequence wherein the wild-type amino acid sequence at one or more of positions 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 218, 219 or 220 is substituted; wherein the BPN' variant has decreased adsorption to, and increased hydrolysis of, an

insoluble substrate as compared to the wild-type subtilisin BPN'. Preferably, the positions having a substituted amino acid are 199, 200, 201, 202, 205, 207, 208, 209, 210, 211, 212, or 215; more preferably, 200, 201, 202, 205 or 207.

Preferred protease enzymes for use according to the present invention also include the subtilisin 309 variants. These protease enzymes include several classes of subtilisin 309 variants.

A. Loop Region 6 Substitution Variants - These subtilisin 309 variants have a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the modified amino acid sequence comprises a substitution at one or more of positions 193, 194, 195, 196, 197, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213 or 214; whereby the subtilisin 309 variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309. Preferably these proteases have amino acids substituted at 193, 194, 195, 196, 199, 201, 202, 203, 204, 205, 206 or 209; more preferably 194, 195, 196, 199 or 200.

B. Multi-Loop Regions Substitution Variants - These subtilisin 309 variants may also be a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the modified amino acid sequence comprises a substitution at one or more positions in one or more of the first, second, third, fourth, or fifth loop regions; whereby the subtilisin 309 variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309.

C. Substitutions at positions other than the loop regions - In addition, one or more substitution of wild-type subtilisin 309 may be made at positions other than positions in the loop regions, for example, at position 74. If the additional substitution to the subtilisin 309 is mad at position 74 alone, the substitution is preferably with Asn, Asp, Glu, Gly, His, Lys, Phe or Pro, preferably His or Asp. However modifications can be made to one or more loop positions as well as position 74, for example residues 97, 99, 101, 102, 105 and 121.

Subtilisin BPN' variants and subtilisin 309 variants are further described in WO 95/29979, WO 95/30010 and WO 95/30011, all of which were published November 9, 1995, all of which are incorporated herein by reference.

Lipases - Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. Other suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase is available from

Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Further suitable lipases are lipases such as MI Lipase^R and Lipomax^R (Gist-Brocades). Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE[®] enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Highly preferred lipases are the D96L lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in US Serial No. 08/341,826. (See also patent application WO 92/05249 viz. wherein the native lipase ex *Humicola lanuginosa* aspartic acid (D) residue at position 96 is changed to Leucine (L). According to this nomenclature said substitution of aspartic acid to Leucine in position 96 is shown as : D96L.) Preferably the *Humicola lanuginosa* strain DSM 4106 is used.

In spite of the large number of publications on lipase enzymes, only the lipase derived from *Humicola lanuginosa* and produced in *Aspergillus oryzae* as host has so far found widespread application as additive for fabric washing products. It is available from Novo Nordisk under the tradename Lipolase[™], as noted above. In order to optimize the stain removal performance of Lipolase, Novo Nordisk have made a number of variants. As described in WO 92/05249, the D96L variant of the native *Humicola lanuginosa* lipase improves the lard stain removal efficiency by a factor 4.4 over the wild-type lipase (enzymes compared in an amount ranging from 0.075 to 2.5 mg protein per liter). Research Disclosure No. 35944 published on March 10, 1994, by Novo Nordisk discloses that the lipase variant (D96L) may be added in an amount corresponding to 0.001-100- mg (5-500,000 LU/liter) lipase variant per liter of wash liquor.

Lipase enzyme is incorporated into the composition in accordance with the invention at a level of from 50 LU to 8500 LU per liter wash solution. Preferably the variant D96L is present at a level of from 100 LU to 7500 LU per liter of wash solution. More preferably at a level of from 150 LU to 5000 LU per liter of wash solution.

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of

cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

Cellulase Enzymes - The laundry detergent compositions according to the present invention may further comprise at least 0.001% by weight, preferably at least about 0.01%, of a cellulase enzyme. However, an effective amount of cellulase enzyme is sufficient for use in the laundry detergent compositions described herein. The term "an effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. The compositions herein will typically comprise from about 0.05% to about 2%, preferably from about 0.1% to about 1.5% by weight of a commercial enzyme preparation. The cellulase enzymes of the present invention are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Preferably, the optimum pH of the enzyme-containing composition is between about 7 and about 9.5.

U. S. Patent No. 4,435,307, Barbsgaard et al, issued March 6, 1984, discloses cellulase produced from *Humicola insolens*. Examples of other suitable cellulases include those produced by a strain of *Humicola insolens*, *Humicola grisea* var. *thermoidea*, and cellulases produced by a species of *Bacillus* sp. or *Aeromonas* sp. Other useful cellulases are those extracted from the hepatopancreas of the marine mollusc *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in the following: GB 2,075,028 A (Novo Industri A/S); GB 2,095,275 A (Kao Soap Co., Ltd.); and Horikoshi et al, U.S. Patent No. 3,844,890 (Rikagaku Kenkyusho). In addition, suitable cellulases and methods for their preparation are described in PCT International Publication Number WO 91/17243, published November 14, 1991, by Novo Nordisk A/S.

Cellulases are known in the art and can be obtained from suppliers under the tradenames: Celluzyne®, Endolase®, and Carezyme®.

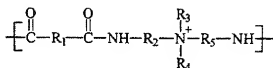
For industrial production of the cellulases herein it is preferred that recombinant DNA techniques be employed. However other techniques involving adjustments of fermentations or mutation of the microorganisms involved can be employed to ensure overproduction of the desired enzymatic activities. Such methods and techniques are known in the art and may readily be carried out by persons skilled in the art.

Polyamide-Polyamine Materials - Another optional but preferred component of the detergent compositions herein comprises one or more polyamide-polyamine materials fabric treatment agents. Such materials, especially when combined with the modified polyamine fabric appearance agents of this invention, have been found to impart a

number of appearance benefits to fabrics and textiles laundered in aqueous washing solutions formed from detergent compositions which contain such combinations. These fabric appearance benefits can include, for example, improved overall appearance of the laundered fabrics, reduction of the formation of pills and fuzz, protection against color fading, etc. The polyamine-polyamide polymers used in the compositions and methods herein can provide such fabric appearance benefits with acceptably little or no loss in cleaning performance provided by the laundry detergent compositions into which such materials are incorporated.

The polyamide-polyamines useful herein will generally comprise from about 0.1% to 8% by the weight of the composition. More preferably, such polyamide-polyamine materials will comprise from about 0.5% to 4% by weight of the compositions herein. Most preferably, these polyamide-polyamines will comprise from about 1% to 3% by weight of the composition.

The polyamide-polyamine materials used in this invention are those which have repeating, substituted amido-amine units which correspond to the general Structural Formula No. I as follows:



Structural Formula No. I

In Structural Formula No. I, R₁, R₂ and R₅ are each independently C₁₋₄ alkylene, C₁₋₄ alkylene or arylene. It is also possible to eliminate R₁ entirely so that the polyamide-polyamine is derived from oxalic acid.

Also in Structural Formula No. I, R₃ is H, epichlorohydrin, an azetidinium group, an epoxypropyl group or a dimethylaminohydroxypropyl group, and R₄ can be H, C₁₋₄ alkyl, C₁₋₄ alkaryl, or aryl. R₄ may also be any of the foregoing groups condensed with C₁₋₄ alkylene oxide.

R₁ is preferably butylene, and R₂ and R₅ are preferably ethylene. R₃ is preferably epichlorohydrin. R₄ is preferably H.

The polyamide-polyamine materials useful herein can be prepared by reacting polyamines such as diethylenetriamine, triethylenetetraamine, tetraethylenepentamine or dipropylenetriamine with C₂-C₁₂ dicarboxylic acids such as oxalic, succinic, glutaric, adipic and diglycolic acids. Such materials may then be further derivatized by reaction with, for example, epichlorohydrin. Preparation of such materials is described in greater

detail in Keim, U.S. Patent 2,296,116, Issued February 23, 1960; Keim, U.S. Patent 2,296,154, Issued February 23, 1960 and Keim, U.S. Patent 3,332,901, Issued July 25, 1967. The disclosures of all three of these patents are incorporated herein by reference.

The polyamide-polyamine-epichlorohydrin fabric treatment agents preferred for use herein are commercially marketed by Hercules, Inc. under the tradename Kymene®. Especially useful are Kymene 557H® and Kymene 557LX® which are epichlorohydrin adducts of polyamide-polyamines which are the reaction products of diethylenetriamine and adipic acid. Other suitable materials are those marketed by Hercules under the tradenames Reten® and Delsette®, and by Sandoz under the tradename Cartaretin®. These polyamide-polyamine materials are marketed in the form of aqueous suspensions of the polymeric material containing, for example, about 12.5% by weight of solids.

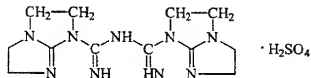
Dye Fixative Materials - optionally but preferred for use herein are selected dye fixative materials which do not form precipitates with anionic surfactant. Such non-precipitating dye fixative materials, particularly in combination with the modified polyamine fabric appearance agents of this invention, have been found to dye fixative benefits to fabrics and textiles laundered in aqueous washing solutions formed from detergent compositions which contain such dye fixatives. Additional benefits from the combination of these dye fixative materials and the modified polyamine fabric appearance agents of this invention can include, for example, improved overall appearance of the laundered fabrics and protection against color fading. The selected dye fixatives used in the compositions and methods herein can provide such fabric appearance benefits with acceptably little or no loss in cleaning performance provided by the laundry detergent compositions into which such materials are incorporated.

The selected dye fixatives useful herein may be in the form of unpolymerized materials, oligomers or polymers. Moreover, the preferred dye fixatives useful herein are cationic. The dye fixative component of the compositions herein will generally comprise from about 0.1% to 5% by the weight of the composition. More preferably, such dye fixative materials will comprise from about 0.5% to 4% by weight of the compositions, most preferably from about 1% to 3%. Such concentrations should be sufficient to provide from about 10 to 100 ppm of the dye fixative in the aqueous washing solutions formed from the laundry detergent compositions herein. More preferably from about 20 to 60 ppm of the dye fixative will be delivered to the aqueous washing solution, most preferably about 50 ppm.

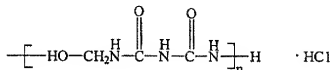
The non-precipitating dye fixatives useful herein include a number that are commercially marketed by CLARIANT Corporation under the Sandofix®, Sandolec® and Polymer VRN® tradenames. These include, for example, Sandofix SWE®,

Sandofix WA[®], Sandolec CT[®], Sandolec CS[®], Sandolec CI[®], Sandolec CF[®], Sandolec WA[®] and Polymer VRN[®]. Other suitable dye fixatives are marketed by Ciba-Geigy Corporation under the tradename Cassofix FRN-300[®] and by Hoechst Celanese Corporation under the tradename Tinofix EW[®].

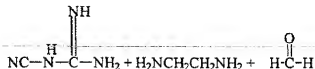
A preferred non-precipitating dye fixative is the Sandofix SWE[®] material which has the structure:



Another preferred non-precipitating dye fixative is the Sandofix WA[®] material which is polymer having the following structure:



Another preferred non-precipitating dye fixative is the Cassofix FRN-300[®] material which is also a polymer prepared from the following monomers:



The dye fixative materials used in this invention are generally all water-soluble materials. They can therefore be utilized for detergent composition preparation in the form of aqueous solutions of such dye fixatives if desired.

Alkyl alkoxyated sulfates and/or alkyl sulfates - The alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula $\text{RO}(\text{A})_m\text{SO}_3\text{M}$ wherein R is an unsubstituted C_{10} - C_{24} alkyl or hydroxyalkyl group having a C_{10} - C_{24} alkyl component, preferably a C_{12} - C_{18} alkyl or hydroxyalkyl, more preferably C_{12} - C_{15} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxyated sulfates as well as alkyl propoxyated sulfates are contemplated herein.

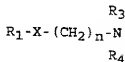
Specific examples of substituted ammonium cations include ethanol-, triethanol-, methyl-, dimethyl-, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C₁₂-C₁₅ alkyl polyethoxylate (1.0) sulfate (C₁₂-C₁₅E(1.0)M), C₁₂-C₁₅ alkyl polyethoxylate (2.25) sulfate (C₁₂-C₁₅E(2.25)M), C₁₂-C₁₅ alkyl polyethoxylate (3.0) sulfate (C₁₂-C₁₅E(3.0)M), and C₁₂-C₁₅ alkyl polyethoxylate (4.0) sulfate (C₁₂-C₁₅E(4.0)M), wherein M is conveniently selected from sodium and potassium.

The alkyl sulfate surfactants hereof are water soluble salts or acids of the formula ROSO₃M wherein R preferably is a C₈-C₁₈ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C₁₀-C₁₈ alkyl component, more preferably a C₁₂-C₁₅ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

Commercial alkyl alkoxyate sulfates comprise a mixture of compounds with varying degrees of alkoxylation. For example, C₁₂-15 polyoxyethylene (3) sulfate from Shell Chemical Company, Houston, TX, will contain molecules with from zero ethoxylates to five or more, for an average degree of ethoxylation = 3. The lower the average degree of ethoxylation of a given sample, the higher the level of alkyl sulfate (EO=0) which may be present in the mixture.

For purposes of this invention, the total amount of alkyl sulfate present in the detergent compositions herein include not only the alkyl sulfate added to the composition but also any alkyl sulfate which may be present in the alkyl alkoxyate sulfate surfactant mixture.

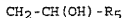
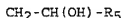
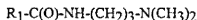
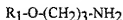
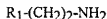
The amine - Suitable amine surfactants for use herein include amines according to the formula:



wherein R₁ is a C₆-C₁₂ alkyl group; n is from about 2 to about 4, X is a bridging group which is selected from NH, CONH, COO, or O or X can be absent; and R₃ and R₄ are

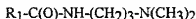
individually selected from H, C₁-C₄ alkyl, or (CH₂-CH₂-O(R₅)) wherein R₅ is H or methyl.

Preferred amines include the following:



wherein R₁ is a C₆-C₁₂ alkyl group and R₅ is H or CH₃.

In a highly preferred embodiment, the amine is described by the formula:



wherein R₁ is C₈-C₁₂ alkyl.

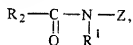
Particularly preferred amines include those selected from the group consisting of octyl amine, hexyl amine, decyl amine, dodecyl amine, C₈-C₁₂ bis(hydroxyethyl)amine, C₈-C₁₂ bis(hydroxyisopropyl)amine, and C₈-C₁₂ amido-propyl dimethyl amine, and mixtures.

Deterative Surfactants - Nonlimiting examples of anionic surfactants useful herein typically at levels of at least about 0.1%, preferably from about 0.1% to about 95%, more preferably from about 1% to about 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS"), primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺)CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺)CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alpha-sulfonated fatty acid esters, the C₁₀-C₁₈ sulfated alkyl polyglycosides, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AES"; especially EO 1-7 ethoxy sulfates), and C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates). The C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Other conventional useful surfactants are listed in standard texts.

Nonionic Surfactants - Nonlimiting examples of nonionic surfactants useful herein typically at levels of at least about 0.1%, preferably from about 0.1% to about 95%, more preferably from about 1% to about 55%, by weight, include the alkoxylated alcohols (AE's) and alkyl phenols, polyhydroxy fatty acid amides (PFAA's), alkyl polyglycosides (APG's), C₁₀-C₁₈ glycerol ethers, and the like.

More specifically, the condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide (AE) are suitable for use as the nonionic surfactant in the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 1 to about 10 moles, preferably 2 to 7, most preferably 2 to 5, of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include: Tergitol™ 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide) and Tergitol™ 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol™ 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), Neodol™ 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3 moles of ethylene oxide), Neodol™ 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide) and Neodol™ 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company; Kyro™ EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company; and Genapol LA O3O or O5O (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. The preferred range of HLB in these AE nonionic surfactants is from 8-11 and most preferred from 8-10. Condensates with propylene oxide and butylene oxides may also be used.

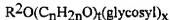
Another class of preferred nonionic surfactants for use herein are the polyhydroxy fatty acid amide surfactants of the formula.



wherein R¹ is H, or C₁₋₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an

alkoxylated derivative thereof. Typical examples include the C₁₂-C₁₈ and C₁₂-C₁₄ N-methylglucamides. See U.S. 5,194,639 and 5,298,636. N-alkoxy polyhydroxy fatty acid amides can also be used; see U.S. 5,489,393.

Also useful as the nonionic surfactant in the present invention are the alkylpolysaccharides such as those disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms. The preferred alkylpolyglycosides have the formula



wherein R² is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are also suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant in the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. Examples of compounds of this type include certain of the commercially-available PluronicTM surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Builders - Detergent builders can optionally but preferably be included in the compositions herein, for example to assist in controlling mineral, especially Ca and/or Mg, hardness in wash water or to assist in the removal of particulate soils from surfaces. Builder level can vary widely depending upon end use and physical form of the composition. Built detergents typically comprise at least about 1% builder. Liquid

formulations typically comprise about 5% to about 50%, more typically 5% to 35% of builder. Lower or higher levels of builders are not excluded. For example, certain detergent additive or high-surfactant formulations can be unbuilt.

A preferred builder for use herein are citrates, e.g., citric acid and soluble salts thereof. It is believed that the combination of polyamine fabric appearance agents of this invention in combination with citrate builder provides increase levels of cleaning. Thus, in one embodiment of the present invention, the detergent composition comprises from about 1% to about 10%, more preferably from about 2% to about 8%, still more preferably from about 4% to about 7%, by weight of citrate builder.

Suitable builders herein can be selected from the group consisting of phosphates and polyphosphates, especially the sodium salts; silicates including water-soluble and hydrous solid types and including those having chain-, layer-, or three-dimensional-structure as well as amorphous-solid or non-structured-liquid types; carbonates, bicarbonates, sesquicarbonates and carbonate minerals other than sodium carbonate or sesquicarbonate; aluminosilicates; organic mono-, di-, tri-, and tetracarboxylates especially water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylates including aliphatic and aromatic types; and phytic acid. These may be complemented by borates, e.g., for pH-buffering purposes, or by sulfates, especially sodium sulfate and any other fillers or carriers which may be important to the engineering of stable surfactant and/or builder-containing detergent compositions.

Builder mixtures, sometimes termed "builder systems" can be used and typically comprise two or more conventional builders, optionally complemented by chelants, pH-buffers or fillers, though these latter materials are generally accounted for separately when describing quantities of materials herein.

P-containing detergent builders often preferred where permitted by legislation include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates exemplified by the tripolyphosphates, pyrophosphates, glassy polymeric meta-phosphates; and phosphonates.

Suitable silicate builders include alkali metal silicates, particularly those liquids and solids having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1, including, particularly for automatic dishwashing purposes, solid hydrous 2-ratio silicates marketed by PQ Corp. under the tradename BRITESIL®, e.g., BRITESIL H2O; and layered silicates, e.g., those described in U.S. 4,664,839, May 12, 1987, H. P. Rieck. See preparative methods in German DE-A-3,417,649 and DE-A-3,742,043.

Also suitable for use herein are synthesized crystalline ion exchange materials or hydrates thereof as taught in U.S. 5,427,711, Sakaguchi et al, June 27, 1995.

Suitable carbonate builders include alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are especially useful in granular detergents, but can also be incorporated in liquids. Suitable for the present purposes are those having empirical formula: $[M_z(AlO_2)_z(SiO_2)_v] \cdot xH_2O$ wherein z and v are integers of at least 6, the molar ratio of z to v is in the range from 1.0 to 0.5, and x is an integer from 15 to 264. Aluminosilicates can be crystalline or amorphous, naturally-occurring or synthetically derived. An aluminosilicate production method is in U.S. 3,985,669, Krummel, et al, October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials are available as Zeolite A, Zeolite P (B), Zeolite X and, to whatever extent this differs from Zeolite P, the so-called Zeolite MAP.

Suitable organic detergent builders include polycarboxylate compounds, including water-soluble nonsurfactant dicarboxylates and tricarboxylates. More typically builder polycarboxylates have a plurality of carboxylate groups, preferably at least 3 carboxylates. Carboxylate builders can be formulated in acid, partially neutral, neutral or overbased form. When in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. Polycarboxylate builders include the ether polycarboxylates, such as oxydisuccinate, see Berg, U.S. 3,128,287, April 7, 1964, and Lamberti et al, U.S. 3,635,830, January 18, 1972; "TMS/TDS" builders of U.S. 4,663,071, Bush et al, May 5, 1987; and other ether carboxylates including cyclic and alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other suitable builders are the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether; 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid; carboxymethyloxysuccinic acid; the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid; as well as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Oxydisuccinates are also especially useful in such compositions and combinations.

Certain deterative surfactants or their short-chain homologs also have a builder action. For unambiguous formula accounting purposes, when they have surfactant capability, these materials are summed up as deterative surfactants. Preferred types for builder functionality are illustrated by: 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the

related compounds disclosed in U.S. 4,566,984, Bush, January 28, 1986. Succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. Succinate builders also include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Lauryl-succinates are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986. Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions as surfactant/builder materials alone or in combination with the aforementioned builders, especially citrate and/or the succinate builders, to provide additional builder activity. Other suitable polycarboxylates are disclosed in U.S. 4,144,226, Crutchfield et al, March 13, 1979 and in U.S. 3,308,067, Diehl, March 7, 1967. See also Diehl, U.S. 3,723,322.

Other types of inorganic builder materials which can be used have the formula $(M_x)_i Ca_y (CO_3)_z$ wherein x and i are integers from 1 to 15, y is an integer from 1 to 10, z is an integer from 2 to 25, M_i are cations, at least one of which is a water-soluble, and the equation $\sum_i = 1 - 15(x_i \text{ multiplied by the valence of } M_i) + 2y = 2z$ is satisfied such that the formula has a neutral or "balanced" charge. These builders are referred to herein as "Mineral Builders".

Enzyme Stabilizing System - The enzyme-containing compositions herein may optionally also comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergent enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

Another stabilizing approach is by use of borate species. See Severson, U.S. 4,537,706.

Stabilizing systems of certain cleaning compositions may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine

(MEA), and mixtures thereof can likewise be used. Likewise, special enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired.

Polymeric Soil Release Agent - Known polymeric soil release agents, hereinafter "SRA" or "SRA's", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the composition.

SRA's can include a variety of charged, e.g., anionic or even cationic (see U.S. 4,956,447), as well as noncharged monomer units and structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. See U.S. 4,711,730, December 8, 1987 to Gosselink et al, for examples of those produced by transesterification/ oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, Me-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al.

SRA's also include simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulose derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; and the C₁-C₄ alkylcelluloses and C₄ hydroxyalkyl celluloses;

see U.S. 4,000,093, December 28, 1976 to Nicol, et al. Suitable SRA's characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate), grafted onto polyalkylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available examples include SOKALAN SRA's such as SOKALAN HP-22, available from BASF, Germany. Other SRA's are polyesters with repeat units containing 10-15% by weight of ethylene terephthalate together with 90-80% by weight of polyoxyethylene terephthalate, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Commercial examples include ZELCON 5126 from Dupont and MILEASE T from ICI.

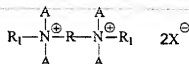
U.S. 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995. Suitable monomers for the above SRA include Na 2-(2-hydroxyethoxy)-ethanesulfonate, DMT, Na- dimethyl 5-sulfoisophthalate, EG and PG.

Additional classes of SRA's include (I) nonionic terephthalates using diisocyanate coupling agents to link up polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al; (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With a proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.; (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al; (IV) poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate, including both nonionic and cationic polymers, see U.S. 4,579,681, Ruppert et al.; (V) graft copolymers, in addition to the SOKALAN types from BASF made, by grafting acrylic monomers on to sulfonated polyesters; these SRA's assertedly have soil release and anti-redeposition activity similar to known cellulose ethers: see EP 279,134 A, 1988, to Rhone-Poulenc Chemie; (VI) grafts of vinyl monomers such as acrylic acid and vinyl acetate on to proteins such as caseins, see EP 457,205 A to BASF (1991); (VII) polyester-polyamide SRA's prepared by condensing adipic acid, caprolactam, and polyethylene glycol, especially for treating polyamide fabrics, see Bevan et al, DE 2,335,044 to Unilever N. V., 1974. Other useful SRA's are described in U.S. Patents 4,240,918, 4,787,989, 4,525,524 and 4,877,896.

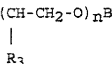
Clay Soil Removal/Anti-redeposition Agents - The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Liquid detergent compositions which contain these compounds typically contain from about 0.01% to about 5% by weight of the water-soluble ethoxylates amines.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylene-pentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. See U.S. Patent 4,891,160, VanderMeer, issued January 2, 1990 and WO 95/32272, published November 30, 1995. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Optionally, but preferred antiredeposition agents useful for this invention are alkoxyated quaternary diamines of the general formula:

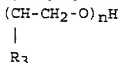


where R is selected from linear or branched C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, [(CH₂CH₂O)_qCH₂CH₂]- and -CH₂CH(OH)CH₂O-(CH₂CH₂O)_qCH₂CH(OH)CH₂]- where q is from about 1 to about 100. Each R₁ is independently selected from C₁-C₄ alkyl, C₇-C₁₂ alkylaryl, or A. A is of the formula:



where R₃ is selected from H or C₁-C₃ alkyl, n is from about 5 to about 100, and B is selected from H, C₁-C₄ alkyl, acetyl, or benzoyl; X is a water soluble anion.

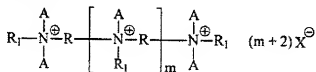
In preferred embodiments, R is selected from C₄ to C₈ alkylene, R₁ is selected from C₁-C₂ alkyl or C₂-C₃ hydroxyalkyl, and A is:



where R₃ is selected from H or methyl, and n is from about 10 to about 50.

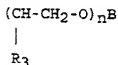
In another preferred embodiment R is linear or branched C₆, R₁ is methyl, R₃ is H, and n is from about 20 to about 50.

Another optional but preferred antideposition agent is alkoxyated quaternary polyamines of the general formula:



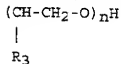
where R is selected from linear or branched C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, [(CH₂CH₂O)_qCH₂CH₂]- and -CH₂CH(OH)CH₂O-(CH₂CH₂O)_qCH₂CH(OH)CH₂]- where q is from about 1 to about 100. If present, Each R₁ is independently selected from C₁-C₄ alkyl, C₇-C₁₂ alkylaryl, or A. R₁ may be absent on some nitrogens; however, at least three nitrogens must be quaternized.

A is of the formula:



where R₃ is selected from H or C₁-C₃ alkyl, n is from about 5 to about 100, and B is selected from H, C₁-C₄ alkyl, acetyl, or benzoyl; m is from about 1 to about 4, and X is a water soluble anion.

In preferred embodiments, R is selected from C₄ to C₈ alkylene, R₁ is selected from C₁-C₂ alkyl or C₂-C₃ hydroxyalkyl, and A is:



where R₃ is selected from H or methyl, and n is from about 10 to about 50; and m is 1.

In another preferred embodiment R is linear or branched C₆, R₁ is methyl, R₃ is H, and n is from about 20 to about 50, and m is 1.

These antiredeposition agents can be synthesized following the methods outline in U.S. Patent No. 4,664,848, or other ways known to those skilled in the art.

The levels of the redeposition agents used to prepare finished laundry detergent compositions can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The

ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Brightener - Any optical brighteners or other brightening agents known in the art can be incorporated at levels typically from about 0.01% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, the 2-(4-styryl-phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)biphenyls; and the aminocoumarins. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.

Dye Transfer Inhibiting Agents - The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: $-NC(O)-$, $-C(O)O-$, $-S-$, $-O-$, $-N=$; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a poly-vinyl-pyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example,

EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morpholino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morpholino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanol diglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Suds Suppressors - Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbon chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as

paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

Alkoxyated Polycarboxylates - Alkoxyated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et

seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxyated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

Perfumes - Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 2%, by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Non-limiting examples of perfume ingredients useful herein include: 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; ionone methyl; ionone gamma methyl; methyl cedrylone; methyl dihydrojasmonate; methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; para-hydroxy-phenyl-butanone; benzophenone; methyl beta-naphthyl ketone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecane; condensation products of hydroxycitronellal and methyl anthranilate, condensation products of hydroxycitronellal and indol, condensation products of phenyl acetaldehyde and indol; 2-methyl-3-(para-

tert-butylphenyl)-propionaldehyde; ethyl vanillin; heliotropin; hexyl cinnamic aldehyde; amyl cinnamic aldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; coumarin; decalactone gamma; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; beta-naphthol methyl ether; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; cedrol, 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; tricyclodecyl propionate; tricyclodecyl acetate; benzyl salicylate; cedryl acetate; and para-(tert-butyl) cyclohexyl acetate.

Particularly preferred perfume materials are those that provide the largest odor improvements in finished product compositions containing cellulases. These perfumes include but are not limited to: hexyl cinnamic aldehyde; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethylnaphthalene; benzyl salicylate; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; para-tert-butyl cyclohexyl acetate; methyl dihydro jasmonate; beta-naphthol methyl ether; methyl beta-naphthyl ketone; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gamma-2-benzopyrane; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; anisaldehyde; coumarin; cedrol; vanillin; cyclopentadecanolide; tricyclodecyl acetate; and tricyclodecyl propionate.

Other perfume materials include essential oils, resinoids, and resins from a variety of sources including, but not limited to: Peru balsam, Olibanum resinoid, styrax, labdanum resin, nutmeg, cassia oil, benzoin resin, coriander and lavandin. Still other perfume chemicals include phenyl ethyl alcohol, terpineol, linalool, linalyl acetate, geraniol, nerol, 2-(1,1-dimethylethyl)-cyclohexanol acetate, benzyl acetate, and eugenol. Carriers such as diethylphthalate can be used in the finished perfume compositions.

Other Ingredients - A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, water-soluble magnesium and/or calcium salts such as MgCl₂, MgSO₄, CaCl₂, CaSO₄ and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

A porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C₁₃₋₁₅ ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 10.5. Liquid dishwashing product formulations preferably have a pH between about 6.8 and about 9.0. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

Liquid Detergents

The manufacture of heavy duty liquid detergent compositions, especially those designed for fabric laundering, which comprise a non-aqueous carrier medium can be prepared according to the disclosures of U.S. Patents 4,753,570; 4,767,558; 4,772,413; 4,889,652; 4,892,673; GB-A-2,158,838; GB-A-2,195,125; GB-A-2,195,649; U.S. 4,988,462; U.S. 5,266,233; EP-A-225,654 (6/16/87); EP-A-510,762 (10/28/92); EP-A-540,089 (5/5/93); EP-A-540,090 (5/5/93); U.S. 4,615,820; EP-A-565,017 (10/13/93); EP-A-030,096 (6/10/81), incorporated herein by reference. Such compositions can contain various particulate detergent ingredients stably suspended therein. Such non-aqueous compositions thus comprise a LIQUID PHASE and, optionally but preferably, a SOLID PHASE, all as described in more detail hereinafter and in the cited references. The modified polyamine fabric appearance agents are incorporated in the compositions at

the levels and in the manner described hereinabove for the manufacture of other laundry detergent compositions.

The compositions of this invention can be used to form aqueous washing solutions for use in the laundering of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine, to form such aqueous laundering solutions. The aqueous washing solution so formed is then contacted, preferably under agitation, with the fabrics to be laundered therewith.

An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering solutions can comprise amounts sufficient to form from about 500 to 7,000 ppm of composition in aqueous solution. More preferably, from about 800 to 3,000 ppm of the detergent compositions herein will be provided in aqueous washing solution.

The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

In the following Examples all levels are quoted as % by weight of the composition.

EXAMPLE I

Preparation of PEI 600 E₂₀

The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 250 g portion of polyethyleneimine (PEI) (Nippon Shokubai, having a listed average molecular weight of 600 equating to about 0.417 moles of polymer and 6.25 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any

reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 275 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 135 g of a 25% sodium methoxide in methanol solution (0.625 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of approximately 5225 g of ethylene oxide (resulting in a total of 20 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 60 g methanesulfonic acid (0.625 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

EXAMPLE II

The following describe liquid detergent compositions according to the present invention:

Ingredients	Weight %			
	A	B	C	D
Polyhydroxy coco-fatty acid amide	3.5	3.5	3.5	3.5
NEODOL 23-9 ¹	2.0	2.0	2.0	2.0
C ₂₅ Alkyl ethoxylate sulphate	19.0	19.0	19.0	19.0
C ₂₅ Alkyl sulfate	--	--	3.5	2.0
C ₁₀ -Aminopropylamide	--	0.5	1.5	0.5
Citric acid	3.0	5.0	3.0	5.0
Tallow fatty acid	2.0	--	2.0	--
Ethanol	3.5	3.5	3.5	3.5
Propanediol	6.0	6.0	6.0	6.0
Monomethanol amine	0.5	0.5	0.5	0.5
Sodium hydroxide	3.0	2.5	3.5	2.5
Sodium p-toluene sulfonate	2.5	2.5	2.5	2.5
Borax	2.5	2.5	2.5	2.5
Protease ²	0.8	0.8	0.8	0.8
Lipolase ³	0.1	0.1	0.1	0.1
Duramyl ⁴	0.1	0.1	--	--
α -amylase ⁵	--	--	0.1	0.1
CAREZYME	0.05	0.05	0.05	0.05
Optical Brightener ⁶	0.1	0.1	0.1	0.1
Modified Polyamine ⁷	1.2	1.2	1.2	1.2
Soil release agent ⁸	0.2	0.2	0.2	0.2
Fumed silica	0.1	0.1	0.1	0.1
Minors, aesthetics, water	Balance to 100%			

1. C₁₂-C₁₃ alkyl E9 ethoxylate as sold by Shell Oil Co.
2. *Bacillus amyloliquefaciens* subtilisin as described in WO 95/10615 published April 20, 1995 by Genencor International.
3. Derived from *Humicola lanuginosa* and commercially available from Novo.
4. Disclosed in WO 9510603 A and available from Novo.
5. α -amylase disclosed herein, including TERMAMYL[®], RAPIDASE[®], FUNGAMYL[®], DURAMYL[®].

6. Brightener is selected from Brightener 49 (Tinopal CBS), inopal UNPA, Tinopal CBS, Tinopal 5BM, Artic White CC, Artic White CWD, 2-(4-styryl-phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes, 4,4'-bis(styryl)bisphenyls, and amino-coumarins.
7. PEI 600 E20 as described above.
8. Terephthalate co-polymer as disclosed in U.S. Patent 4,968,451, Scheibel et al., issued November 6, 1990.

EXAMPLE III

The following describe liquid detergent compositions according to the present invention:

Ingredients	Weight %		
	A	B	C
Polyhydroxy coco-fatty acid amide	3.5	3.5	--
NEODOL 23-9 ¹	2.0	2.0	2.0
C ₂₅ Alkyl ethoxylate sulphate	15.0	15.0	15.0
C ₂₅ Alkyl sulfate	2.0	2.0	--
C ₁₀ -Aminopropylamide	--	--	0.5
Linear alkylbenzene sulfonate	4.0	4.0	4.0
Citric acid	3.0	5.0	5.0
Tallow fatty acid	2.0	2.0	2.0
Ethanol	3.4	3.4	3.4
Propanediol	6.0	6.0	6.0
Monomethanol amine	0.5	0.5	0.5
Sodium hydroxide	3.0	2.5	2.5
Sodium p-toluene sulfonate	2.5	2.5	2.5
Borax	2.5	2.5	2.5
Protease ²	0.8	0.8	0.8
Lipolase ³	0.1	0.1	0.1
α -amylase ⁵	0.1	0.1	0.1
CAREZYME	0.05	0.05	0.05
Optical Brightener	0.1	0.1	0.1
Modified Polyamine ⁶	1.2	1.2	1.2

Ethoxylated tetraethylene-pentamine	3.0	3.0	3.0
Soil release agent ⁷	0.2	0.2	0.2
Fumed silica	0.1	0.1	0.1
Acrylic acid/maleic acid co-polymer	--	--	0.05
Ethylenediamine disuccinate chelant	--	1.0	--
Fabric Integrity agents ⁸	2.0	3.5	0.75
Minors, aesthetics, water	Balance to 100%		

1. C₁₂-C₁₃ alkyl E9 ethoxylate as sold by Shell Oil Co.
2. *Bacillus amyloliquefaciens* subtilisin as described in WO 95/10615 published April 20, 1995 by Genencor International.
3. Derived from *Humicola lanuginosa* and commercially available from Novo.
5. α -amylase disclosed herein, including TERMAMYL[®], RAPIDASE[®], FUNGAMYL[®], DURAMYL[®].
6. PEI 600 E₂₀ as described above.
7. Terephthalate co-polymer as disclosed in U.S. Patent 4,968,451, Scheibel et al., issued November 6, 1990.
8. Fabric integrity agents selected from prill/fuzz reduction agents, antiredeposition agents, antifading agents, dye fixatives, and mixtures thereof.

Ingredients	Weight %		
	D	E	F
Polyhydroxy coco-fatty acid amide	4.0	5.0	5.0
NEODOL 23-9 ¹	4.0	4.0	2.0
C ₂₅ Alkyl ethoxylate sulphate	4.0	17.0	25.0
C ₂₅ Alkyl sulfate	14.0	7.0	-
C ₁₀ -Aminopropylamide	1.0	2.0	1.0
Linear alkylbenzene sulfonate	--	--	4.0
Citric acid	5.0	5.0	5.0
Tallow fatty acid	7.0	5.0	5.0
Ethanol	2.0	5.5	10.0
Propanediol	9.0	8.0	8.0

Monomethanol amine	5.0	9.0	7.0
Sodium hydroxide	2.0	1.5	0.5
Sodium p-toluene sulfonate	0.1	2.0	2.0
Borax	2.0	3.5	3.5
Protease ²	0.2	1.5	1.5
Lipolase ³	0.06	0.2	--
α -amylase ⁵	0.2	0.1	0.1
CAREZYME	--	0.1	0.1
Optical Brightener	0.15	0.1	0.1
Modified Polyamine ⁶	1.2	1.2	1.2
Ethoxylated tetraethylene-pentamine	1.0	3.0	3.0
Soil release agent ⁷	0.2	0.5	0.5
Fumed silica	0.2	0.1	--
Acrylic acid/maleic acid co-polymer	0.05	-	--
Ethylenediamine disuccinate chelant	1.0	0.5	--
Fabric Integrity agents ⁸	1.0	1.5	--
Minors, aesthetics, water	Balance to 100%		

1. C₁₂-C₁₃ alkyl E9 ethoxylate as sold by Shell Oil Co.
2. *Bacillus amyloliquefaciens* subtilisin as described in WO 95/10615 published April 20, 1995 by Genencor International.
3. Derived from *Humicola lanuginosa* and commercially available from Novo.
5. α -amylase disclosed, including TERMAMYL[®], RAPIDASE[®], FUNGAMYL[®], DURAMYL[®].
6. PEI 600 E₂₀ as described above.
7. Terephthalate co-polymer as disclosed in U.S. Patent 4,968,451, Scheibel et al., issued November 6, 1990.
8. Fabric integrity agents selected from prill/fuzz reduction agents, antiredeposition agents, antifading agents, dye fixatives, and mixtures thereof.

EXAMPLE IV

The following describe structured liquid detergent compositions according to the present invention:

Weight %

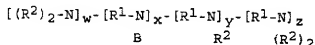
Ingredients	A	B
NEODOL 45-7 ¹	2.0	2.0
C ₂₅ Alkyl ethoxylate sulphate	16.0	16.0
C ₂₅ Alkyl sulfate	--	--
Cationic surfactant ²	5.0	4.0
C12-16 alkyl dimethyl aminoxide	--	1.0
Citric acid	5.0	5.0
Ethanol	--	--
Propanediol	6.4	2.0
Monomethanol amine	--	0.5
Sodium hydroxide	to pH 8.0	to pH 6.7
Borax	2.0	1.0
Protease ³	0.5	1.0
Lipolase ⁴	0.06	0.2
α -amylase ⁵	1.2	0.5
CAREZYME	--	0.5
Optical Brightener	0.2	0.1
Modified Polyamine ⁶	1.0	1.5
Fabric Integrity Agent ⁷	1.0	3.0
Soil release agent ⁸	0.2	0.5
Fumed silica	0.2	0.1
Acrylic acid/maleic acid co-polymer	0.05	-
Ethylenediamine disuccinate chelant	1.0	0.5
Minors, aesthetics, water	Balance to 100%	

1. C₁₄-C₁₅ alkyl E7 ethoxylate as sold by Shell Oil Co.
2. Lauryl trimethyl ammonium chloride
3. *Bacillus amyloliquefaciens* subtilisin as described in WO 95/10615 published April 20, 1995 by Genencor International.
3. Derived from *Humicola lanuginosa* and commercially available from Novo.
5. α -amylase disclosed herein, including TERMAMYL®, RAPIDASE®, FUNGAMYL®, DURAMYL®.
6. PEI 600 E₂₀ as described above.

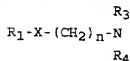
7. Fabric integrity agents selected from prill/fuzz reduction agents, antiredeposition agents, antifading agents, dye fixatives, and mixtures thereof.
8. Terephthalate co-polymer as disclosed in U.S. Patent 4,968,451, Scheibel et al., issued November 6, 1990.

WHAT IS CLAIMED IS:

1. A liquid laundry detergent composition comprising:
 - a) at least 0.1% by weight, of deterative anionic and nonionic surfactants selected from one or more of the following alkyl sulfates, alkyl alkoxy sulfates, linear alkylbenzene sulfonates, polyhydroxy fatty acid amides, and mixtures thereof;
 - b) at least 0.05% by weight, of a water-soluble or dispersible, modified polyamine fabric appearance agent, said agent comprising a polyamine backbone corresponding to the formula:



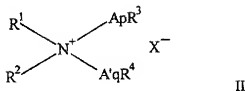
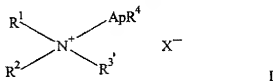
- wherein each R^1 is independently C_2 - C_5 alkylene, alkenylene or arylene; each R^2 is independently H, or a moiety of formula $OH[(CH_2)_xO]_n$, wherein x is from 1 to 8 and n is from 10 to 50; w is 0 or 1; $x+y+z$ is from 5 to 30; and B represents a continuation of this structure by branching; and wherein said polyamine before alkylation has an average molecular weight of from 300 to 1,200; and
- c) one or more additional deterative additives selected from the group consisting of α -amylase, deterative amine, cationic surfactants, antiredeposition agents, antifading agent, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof; and wherein said deterative amine is of the formula:



wherein R_1 is a C_6 - C_{12} alkyl group; n is from 2 to 4, X is a bridging group which is selected from NH, CONH, COO, or O or X can be absent; and R_3 and R_4 are individually selected from H, C_1 - C_4 alkyl, or $(CH_2-CH_2-O(R_5))$ wherein R_5 is H or methyl.

2. A composition according to Claim 1 wherein the detergent composition additionally comprises adjunct ingredients selected from the group consisting of builders, optical brighteners, soil release polymers, dye transfer inhibitors, polymeric dispersing agents, non-amylase enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, and mixtures thereof.

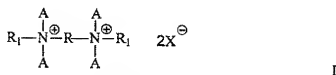
3. A composition according to Claim 2 wherein said adjunct ingredient is a citrate builder; wherein said composition comprises from 2% to 8%, by weight, of said citrate.
4. A composition according to Claim 1 wherein the additional deterative additive is amylase enzyme; wherein said amylase enzyme is selected from the group consisting of:
 - (a) α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α -amylase activity assay;
 - (b) α -amylase showing positive immunological cross-reactivity with antibodies raised against an α -amylase having an amino acid sequence corresponding respectively to those α -amylases in (a); and
 - (c) mixtures thereof.
5. A composition according to Claim 1 wherein said amine is selected from the group consisting of octyl amine, hexyl amine, decyl amine, dodecyl amine, C₈-C₁₂ bis(hydroxyethyl)amine, C₈-C₁₂ bis(hydroxyisopropyl)amine, C₈-C₁₂ amido-propyl dimethyl amine, and mixtures.
6. A composition according to Claim 1 wherein the additional deterative additive is a cationic surfactant of the formula:



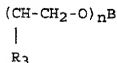
wherein R¹ is an alkyl or alkenyl moiety containing from 8 to 18 carbon atoms;
 R² and R³ are each independently alkyl groups containing from one to about

three carbon atoms; R^3 and R^4 can vary independently and are selected from hydrogen, methyl and ethyl; X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is selected from C_1 - C_4 alkoxy; and for formula I, p is from 2 to 30; and for formula II, p is from 1 to 30 and q is from 1 to 30.

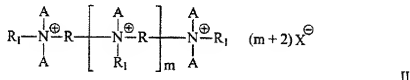
7. A composition according to Claim 1 wherein the additional deterative additive is an antiredeposition agent, said antiredeposition agent is selected from the following formulae:



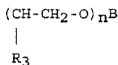
where R is selected from linear or branched C_2 - C_{12} alkylene, C_3 - C_{12} hydroxyalkylene, C_4 - C_{12} dihydroxyalkylene, C_8 - C_{12} dialkylarylene, $[(CH_2CH_2O)_qCH_2CH_2]$ - and $-CH_2CH(OH)CH_2O-$ $(CH_2CH_2O)_qCH_2CH(OH)CH_2]$ - where q is from 1 to 100; each R_1 is independently selected from C_1 - C_4 alkyl, C_7 - C_{12} alkylaryl, or A, wherein A is of the formula:



where R_3 is selected from H or C_1 - C_3 alkyl, n is from 5 to 100, and B is selected from H, C_1 - C_4 alkyl, acetyl, or benzoyl; X is a water soluble anion; and

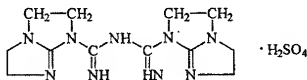


where R is selected from linear or branched C_2 - C_{12} alkylene, C_3 - C_{12} hydroxyalkylene, C_4 - C_{12} dihydroxyalkylene, C_8 - C_{12} dialkylarylene, $[(CH_2CH_2O)_qCH_2CH_2]$ - and $-CH_2CH(OH)CH_2O-$ $(CH_2CH_2O)_qCH_2CH(OH)CH_2]$, where q is from 1 to 100; if present, each R_1 is independently selected from C_1 - C_4 alkyl, C_7 - C_{12} alkylaryl, or A; R_1 may be absent on some nitrogens; however, at least three nitrogens must be quaternized; A is of the formula:



where R_3 is selected from H or C_1 - C_3 alkyl, n is from 5 to 100, and B is selected from H, C_1 - C_4 alkyl, acetyl, or benzoyl; m is from 1 to 4, and X is a water soluble anion.

8. A composition according to Claim 1 wherein the additional deterative additive is an antifading agent comprising from 0.1% to 5% by weight of a dye fixative selected from the group consisting of Cassofix FRN-300[®], Sandofix SWE[®], Sandofix WA[®], Tinofix EW[®], Polymer VRN[®], Sandoec CF[®], Sandoec WA[®], Sandoec CT[®], Sandoec CS[®] and Sandoec Cl[®]; wherein said Sandofix SWE[®] has the formula:



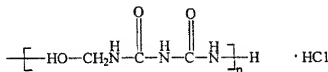
; and wherein said

Cassofix FRN-300[®] polymer is prepared from monomers having the following structures:

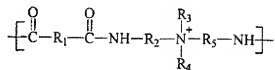


; and wherein said

Sandofix WA[®] polymer has the following structure:



9. A composition according to Claim 1 wherein the additional deterative additive is a pill/fuzz reduction agent comprising from 0.1% to 8% by weight of a polyamide-polyamine fabric treatment agent formed from repeating units of the structural formula:



wherein R₁, R₂, and R₅ are each independently C₁₋₄ alkylene, C₁₋₄ alkarylene or arylene, or wherein R₁ can be eliminated; R₃ is H, epichlorohydrin, an azetidinium group, an epoxypropyl group, or a dimethylaminohydroxypropyl group; and, R₄ is H, C₁₋₄ alkyl, C₁₋₄ alkaryl, or aryl; and said R₄ groups may optionally be condensed with C₁₋₄ alkylene oxide.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/06989

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11B3/37

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 32272 A (PROCTER & GAMBLE) 30 November 1995 cited in the application see page 4, line 10 - page 6, line 34 see page 19, line 1 - page 20, line 35; claims ---	1-3
X	US 4 891 160 A (VANDER MEER JAMES M) 2 January 1990 cited in the application see claims ---	1-3
X	EP 0 206 513 A (PROCTER & GAMBLE ; PROCTER & GAMBLE EUROP (BE)) 30 December 1986 cited in the application see claims ---	1-3

-/-

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (see specification)
 "O" document relating to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
 "&" document member of the same patent family

Date of the actual completion of the international search

26 September 1997

Date of mailing of the international search report

08. 10. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patenlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/US 97/06989

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8920 Derwent Publications Ltd., London, GB; Class D16, AN 89-147480 XP002039752 & JP 01 090 296 A (KAO CORP) , 6 April 1989 see abstract	1-3,5,7
A	DATABASE WPI Section Ch, Week 9606 Derwent Publications Ltd., London, GB; Class A14, AN 96-056303 XP002041928 & JP 07 316 590 A (LION CORP) , 5 December 1995 see abstract	1

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No.

PCT/US 97/06989

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9532272 A	30-11-95	AU 2387095 A	18-12-95
		CA 2189749 A	30-11-95
		EP 0760846 A	12-03-97
		US 5565145 A	15-10-96

US 4891160 A	02-01-90	US 4597898 A	01-07-86
		AU 575034 B	21-07-88
		AU 2280283 A	28-06-84
		CA 1220395 A	14-04-87
		DK 20491 A	06-02-91
		EG 17032 A	30-10-93
		EP 0112593 A	04-07-84
		GB 2133415 A,B	25-07-84
		GB 2175597 A,B	03-12-86
		GB 2180249 A,B	25-03-87
		HK 58390 A	10-08-90
		HK 58790 A	10-08-90
		HK 74590 A	28-09-90
JP 1773204 C	14-07-93		
JP 4054719 B	01-09-92		
JP 59166598 A	19-09-84		

EP 0206513 A	30-12-86	CA 1309925 A	10-11-92



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 17/00, 3/02, 10/04, 1/29	A1	(11) International Publication Number: WO 99/27065 (43) International Publication Date: 3 June 1999 (03.06.99)
<p>(21) International Application Number: PCT/US98/24809</p> <p>(22) International Filing Date: 20 November 1998 (20.11.98)</p> <p>(30) Priority Data: 60/066,567 26 November 1997 (26.11.97) US</p> <p>(71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): SADLOWSKI, Eugene, Steven [US/US]; 9980 Pebbleknoll Drive, Cincinnati, OH 45252 (US).</p> <p>(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).</p>	<p>(81) Designated States: BR, CA, JP, MX, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
(54) Title: AQUEOUS, GEL LAUNDRY DETERGENT COMPOSITION		
(57) Abstract		
<p>An aqueous, heavy duty gel laundry detergent composition comprising anionic surfactants, fatty acids, and specially selected structurants to provide exceptional cleaning benefits and phase stability. The structurant comprises sodium sulfate and optionally conventional detergent builders such as citrate. The anionic surfactants comprise linear alkyl benzene sulfonate, alkyl sulfates and alkyl ethoxylated sulfates.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IS	Iceland	MW	Malawi	UG	Uganda
EY	Belarus	IT	Italy	MX	Mexico	US	United States of America
CA	Canada	JP	Japan	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	KE	Kenya	NL	Netherlands	VN	Viet Nam
CG	Congo	KG	Kyrgyzstan	NO	Norway	YU	Yugoslavia
CH	Switzerland	KP	Democratic People's Republic of Korea	NZ	New Zealand	ZW	Zimbabwe
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

AQUEOUS, GEL LAUNDRY DETERGENT COMPOSITION

Eugene S. Sadowski

TECHNICAL FIELD

The present invention relates to stable, aqueous heavy duty gel laundry detergent compositions comprising anionic surfactants, fatty acids, and specially selected structurants to provide exceptional cleaning benefits and phase stability. The structurant comprises sodium sulfate and optionally, conventional detergent builders such as citrate. The anionic surfactant component comprises linear alkyl benzene sulfonate, alkyl sulfates and alkyl ethoxylated sulfates.

BACKGROUND OF THE INVENTION

The art is replete with examples of laundry detergent compositions which have good cleaning properties. Although many of these are liquids, the formulation of gel detergent compositions present numerous problems to the formulator, including high viscosity at pouring shear rate, instability during storage, unacceptable grease cleaning, and undesirable appearance.

Attempts to formulate gel laundry detergent compositions in the past have included the use of conventional builders such as citrate as structurants. These compositions are gels and have reasonably good phase stability. But builders are expensive and it is often undesirable to formulate a detergent composition with the builder quantities necessary to structure a heavy duty, gel detergent composition. Therefore there is a continuing need for supplemental or replacement structurants for use in aqueous, heavy duty gel detergent compositions which are inexpensive and provide the same or improved structuring.

It has now been found that aqueous, heavy duty gel detergent compositions containing certain anionic surfactants, fatty acid surfactants and certain structurants comprising sodium sulfate provide excellent cleaning performance and attractive product characteristics, i.e., are structured, phase stable, and have a rheology which allows for easy pouring from the product container.

Without being limited by theory, it is believed that these novel compositions have an internal structure which comprises a planar lamellar phase. The presence of such a phase in detergent compositions may be determined by optical or electron microscopy.

SUMMARY OF THE INVENTION

It is an object of the invention herein to provide an aqueous heavy duty gel laundry detergent composition which provides excellent cleaning and a desirable rheology.

The present invention encompasses a heavy duty gel laundry detergent compositions comprising, by weight of the composition:

- a) from about 10% to about 40% of an anionic surfactant system;
- b) from about 5% to about 20% of fatty acids; and
- c) and from about 0.5% to about 6%, preferably from about 2% to about 6%, more preferably from about 3% to about 5%, and most preferably from about 4% to about 5%, of a structurant comprising sodium sulfate.

Preferably the structurant further comprises a detergent builder, which is preferably citrate, in addition to the sodium sulfate. The weight ratio of sodium sulfate to the detergent builder is from about 10:1 to about 1:10, preferably from about 5:1 to about 1:5, more preferably from about 3:1 to about 1:3, and most preferably from about 2:1 to about 1:2. Additional builders suitable for use in the present compositions are carboxylates, polycarboxylates, amino carboxylates, polycarboxylates, carbonates, bicarbonates, phosphates and phosphonates.

The compositions herein may further contain one or more additional deterative additives selected from the group consisting of non-citrate builders, optical brighteners, soil release polymers, dye transfer inhibitors, polymeric dispersing agents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, antiredeposition agents, antifading agent, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof.

The compositions herein have a viscosity at 20 s^{-1} shear rate of from about 100 cp to about 4,000 cp, preferably from about 300 cp to about 3,000 cp, more preferably from about 500 cp to about 2,000 cp and are stable upon storage.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius ($^{\circ}\text{C}$) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has now been found that a stable, aqueous heavy duty gel detergent composition is surprisingly formed when certain anionic surfactants, fatty acid surfactants and structurants comprising sodium sulfate are combined in relative

proportions specified hereinafter. Specifically, a gel laundry detergent composition is defined which comprises, by weight of the composition:

- a) from about 10% to about 40%, by weight of the composition, of an anionic surfactant system;
- b) from about 5% to about 20%, by weight of the composition, of fatty acids; and
- c) and from about 0.5% to about 6%, preferably from about 2% to about 6%, more preferably from about 3% to about 5%, and most preferably from about 4% to about 5%, of a structurant comprising sodium sulfate.

Preferably the structurant further comprises a detergent builder, which is preferably citrate, in addition to the sodium sulfate. The weight ratio of sodium sulfate to the detergent builder is from about 10:1 to about 1:10, preferably from about 5:1 to about 1:5, more preferably from about 3:1 to about 1:3, and most preferably from about 2:1 to about 1:2. Additional builders suitable for use in the present compositions are carboxylates, polycarboxylates, amino carboxylates, polycarboxylates, carbonates, bicarbonates, phosphates and phosphonates. The sodium sulfate is preferably present in the detergent composition from about 0.25% to about 6%, more preferably from about 0.5% to about 5%, even more preferably from about 1% to about 5%, and most preferably from about 3% to about 5%, all percentages are by weight of the detergent composition.

The compositions herein may further contain one or more additional deterative additives selected from the group consisting of non-citrate builders, optical brighteners, soil release polymers, dye transfer inhibitors, polymeric dispersing agents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, antiredeposition agents, antifading agent, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof.

The anionic surfactant system can comprise from about 5% to about 25%, by weight of the composition, of alkyl polyethoxylate sulfates wherein the alkyl group contains from about 10 to about 22 carbon atoms and the polyethoxylate chain contains from about 0.5 to about 15, preferably from about 0.5 to about 5 ethylene oxide moieties. And the composition the detergent composition preferably comprises one or more amine containing deterative materials selected from the group consisting of deterative amines, modified polyamines, polyamide-polyamines, polyethoxylated-polyamine polymers, quaternary ammonium surfactants, and mixtures thereof.

The anionic surfactant system can comprise surfactants selected from the group consisting of linear alkyl benzene sulfonate, alkyl sulfate, alkyl ethoxy sulfate and mixtures thereof.

The compositions herein are structured and have a specific rheology. The rheology can be modeled by the following formula:

$$\eta = \eta_0 + K\dot{\gamma}^{(n-1)}$$

where η is the viscosity of the liquid at a given shear rate, η_0 is the viscosity at infinite shear rate, $\dot{\gamma}$ is the shear rate, n is the shear rate index, and K is the consistency. As used herein, the term "structured" indicates a heavy duty liquid composition having liquid crystalline surfactant particles and an infinite shear viscosity (η_0) value between 0 and about 3,000cp (centipoise), a shear index (n) value of less than about 0.6, a consistency value, K , of above about 1,000, and a viscosity (η) measured at 20^{-1} of less than about 10,000cp, preferably less than about 5,000cp. Under low stress levels, a "zero shear" viscosity is above about 100,000cp wherein "zero shear" is meant a shear rate of 0.001 s^{-1} or less. The yield value of the compositions herein, obtained by plotting viscosity versus stress, is larger than 0.2Pa. These rheology parameters can be measured with any commercially available rheometer, such as the Carrired CSL 100 model.

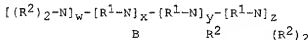
The compositions herein are clear, that is transparent. By "transparent" it is meant that light is easily transmitted through the gel detergent compositions of the present invention and that objects on one side of the gel composition are at least partially visible from the other side of the composition.

Electrolytes - Without being limited by theory, it is believed that the presence of electrolytes acts to control the viscosity of the gel compositions. Thus, the gel nature of the compositions herein are affected by the choice of surfactants and by the amount of electrolytes present. In preferred embodiments herein, the compositions will further comprise from 0% to about 10%, more preferably from about 2% to about 6%, even more preferably from about 3% to about 5%, of a suitable electrolyte or acid equivalent thereof. Sodium citrate is a highly preferred electrolyte for use herein.

The compositions herein may optionally contain from about 0% to about 10%, by weight, of solvents and hydrotropes. Without being limited by theory, it is believed that the presence of solvents and hydrotropes can affect the structured versus isotropic nature of the compositions: By "solvent" is meant the commonly used solvents in the detergent industry, including alkyl monoalcohol, di-, and tri-alcohols, ethylene glycol, propylene glycol, propanediol, ethanediol, glycerine, etc. By "hydrotrope" is meant the commonly used hydrotropes in the detergent industry, including short chain surfactants that help solubilize other surfactants. Other examples of hydrotropes include cumene, xylene, or toluene

sulfonate, urea, C₈ or shorter chain alkyl carboxylates, and C₈ or shorter chain alkyl sulfate and ethoxylated sulfates.

Modified polyamine - The compositions herein may comprise at least about 0.05%, preferably from about 0.05% to about 3%, by weight, of a water-soluble or dispersible, modified polyamine agent, said agent comprising a polyamine backbone corresponding to the formula:

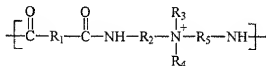


wherein each R¹ is independently C₂-C₅ alkylene, alkenylene or arylene; each R² is independently H, or a moiety of formula OH[(CH₂)_xO]_n, wherein x is from about 1 to about 8 and n is from about 10 to about 50; w is 0 or 1; x+y+z is from about 5 to about 30; and B represents a continuation of this structure by branching; and wherein said polyamine before alkylation has an average molecular weight of from about 300 to about 1,200.

In preferred embodiments, R¹ is C₂-C₄ alkylene, more preferably ethylene; R² is OH[(CH₂CH₂O)]_n, wherein n is from about 15 to about 30, more preferably n is about 20. The average Molecular Weight of the polyamine before alkylation is from about 300 to about 1200, more preferably from about 500 to about 900, still more preferably from about 600 to about 700, even more preferably from about 600 to about 650.

Polyamide-Polyamines - The gel compositions of the present invention preferably comprise from about 0.1% to 8% by the weight of the composition of certain polyamide-polyamines. More preferably, such polyamide-polyamine materials will comprise from about 0.5% to 4% by weight of the compositions herein. Most preferably, these polyamide-polyamines will comprise from about 1% to 3% by weight of the composition.

The polyamide-polyamine materials used in this invention are those which have repeating, substituted amido-amine units which correspond to the general Structural Formula No. 1 as follows:



Structural Formula No. 1

In Structural Formula No. 1, R₁, R₂ and R₅ are each independently C₁₋₄ alkylene, C₁₋₄ alkarylene or arylene. It is also possible to eliminate R₁ entirely so that the polyamide-polyamine is derived from oxalic acid.

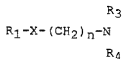
Also in Structural Formula No. 1, R₃ is H, epichlorohydrin, an azetidinium group, an epoxypentyl group or a dimethylaminohydroxypropyl group, and R₄ can be H, C₁₋₄ alkyl, C₁₋₄ alkaryl, or aryl. R₄ may also be any of the foregoing groups condensed with C₁₋₄ alkylene oxide.

R₁ is preferably butylene, and R₂ and R₅ are preferably ethylene. R₃ is preferably epichlorohydrin. R₄ is preferably H.

The polyamide-polyamine materials useful herein can be prepared by reacting polyamines such as diethylenetriamine, triethylenetetraamine, tetraethylenepentamine or dipropylenetriamine with C₂-C₁₂ dicarboxylic acids such as oxalic, succinic, glutaric, adipic and diglycolic acids. Such materials may then be further derivatized by reaction with, for example, epichlorohydrin. Preparation of such materials is described in greater detail in Keim, U.S. Patent 2,296,116, Issued February 23, 1960; Keim, U.S. Patent 2,296,154, Issued February 23, 1960 and Keim, U.S. Patent 3,332,901, Issued July 25, 1967.

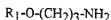
The polyamide-polyamine agents preferred for use herein are commercially marketed by Hercules, Inc. under the tradename Kymene®. Especially useful are Kymene 557H® and Kymene 557LX® which are epichlorohydrin adducts of polyamide-polyamines which are the reaction products of diethylenetriamine and adipic acid. Other suitable materials are those marketed by Hercules under the tradenames Reten® and Delsette®, and by Sandoz under the tradename Cartaretin®. These polyamide-polyamine materials are marketed in the form of aqueous suspensions of the polymeric material containing, for example, about 12.5% by weight of solids.

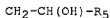
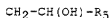
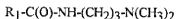
Deterative Amine - Suitable amine surfactants for use herein include deterative amines according to the formula:



wherein R₁ is a C₆-C₁₂ alkyl group; n is from about 2 to about 4, X is a bridging group which is selected from NH, CONH, COO, or O or X can be absent; and R₃ and R₄ are individually selected from H, C₁-C₄ alkyl, or (CH₂-CH₂-O(R₅)) wherein R₅ is H or methyl.

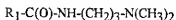
Preferred amines include the following:





wherein R_1 is a C_6 - C_{12} alkyl group and R_5 is H or CH_3 .

In a highly preferred embodiment, the amine is described by the formula:

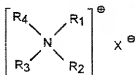


wherein R_1 is C_8 - C_{12} alkyl.

Particularly preferred amines include those selected from the group consisting of octyl amine, hexyl amine, decyl amine, dodecyl amine, C_8 - C_{12} bis(hydroxyethyl)amine, C_8 - C_{12} bis(hydroxyisopropyl)amine, and C_8 - C_{12} amido-propyl dimethyl amine, and mixtures.

If utilized the deterative amines comprise from about 0.1% to about 10%, preferably from about 0.5% to about 5%, by weight of the composition.

Quaternary Ammonium Surfactants - from about 1% to about 6% of a quaternary ammonium surfactant having the formula

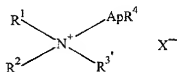


wherein R_1 and R_2 are individually selected from the group consisting of C_1 - C_4 alkyl, C_1 - C_4 hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from about 2 to about 5; X is an anion; and (1) R_3 and R_4 are each a C_6 - C_{14} alkyl or (2) R_3 is a C_6 - C_{18} alkyl, and R_4 is selected from the group consisting of C_1 - C_{10} alkyl, C_1 - C_{10} hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5;

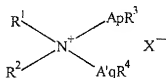
Preferred quaternary ammonium surfactants are the chloride, bromide, and methylsulfate salts. Examples of preferred mono-long chain alkyl quaternary ammonium surfactants are those wherein R_1 , R_2 , and R_4 are each methyl and R_3 is a C_8 - C_{16} alkyl; or wherein R_3 is C_8 - 18 alkyl and R_1 , R_2 , and R_4 are selected from methyl and hydroxy-alkyl moieties. Lauryl trimethyl ammonium chloride, myristyl trimethyl ammonium chloride, palmityl trimethyl ammonium chloride, coconut trimethylammonium chloride, coconut trimethylammonium methylsulfate, coconut dimethyl-monohydroxyethyl-ammonium chloride, coconut dimethyl-monohydroxyethylammonium methylsulfate, steryl dimethyl-monohydroxy-ethylammonium chloride, steryl dimethylmonohydroxy-ethylammonium methylsulfate, di-

C₁₂-C₁₄ alkyl dimethyl ammonium chloride, and mixtures thereof are particularly preferred. ADOGEN 412™, a lauryl trimethyl ammonium chloride commercially available from Witco, is also preferred. Even more highly preferred are the lauryl trimethyl ammonium chloride and myristyl trimethyl ammonium chloride.

Alkoxylated quaternary ammonium (AQA) surfactants useful in the present invention are of the general formula:



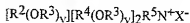
I



II

wherein R¹ is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms; R² and R^{3'} are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl; R³ and R⁴ can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X⁻ is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is selected from C₁-C₄ alkoxy, especially ethoxy (i.e., -CH₂CH₂O-), propoxy, butoxy and mixtures thereof; and for formula I, p is from 2 to about 30, preferably 2 to about 15, most preferably 2 to about 8; and for formula II, p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

Other quaternary surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula:



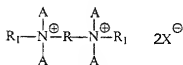
wherein R² is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl, ring

structures formed by joining the two R^4 groups, $-CH_2CHOHCHOHCOR^6CHOH-CH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Polyethoxylated-Polyamine Polymers - Another polymer dispersant form use herein includes polyethoxylated-polyamine polymers (PPP). The preferred polyethoxylated-polyamines useful herein are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's). A common polyalkyleneamine (PAA) is tetrabutyleneamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are trithylenetetramine (TETA) and terathyleneamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

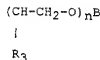
Polyethoxylated polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951

Optionally, but preferred polyethoxylated-polyamine polymers useful for this invention are alkoxyated quaternary diamines of the general formula:



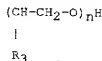
where R is selected from linear or branched C_2-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_8-C_{12} dialkylarylene, $[(CH_2CH_2O)_qCH_2CH_2]-$ and $-CH_2CH(OH)CH_2O-(CH_2CH_2O)_qCH_2CH(OH)CH_2-$ where q is from about 1 to about

100. Each R_1 is independently selected from C_1 - C_4 alkyl, C_7 - C_{12} alkylaryl, or A. A is of the formula:



where R_3 is selected from H or C_1 - C_3 alkyl, n is from about 5 to about 100, and B is selected from H, C_1 - C_4 alkyl, acetyl, or benzoyl; X is a water soluble anion.

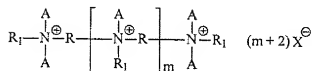
In preferred embodiments, R is selected from C_4 to C_8 alkylene, R_1 is selected from C_1 - C_2 alkyl or C_2 - C_3 hydroxyalkyl, and A is:



where R_3 is selected from H or methyl, and n is from about 10 to about 50.

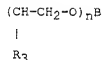
In another preferred embodiment R is linear or branched C_6 , R_1 is methyl, R_3 is H, and n is from about 20 to about 50.

Additional alkoxyated quaternary polyamine dispersants which can be used in the present invention are of the general formula:



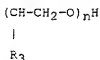
where R is selected from linear or branched C_2 - C_{12} alkylene, C_3 - C_{12} hydroxyalkylene, C_4 - C_{12} dihydroxyalkylene, C_8 - C_{12} dialkylarylene, $[(\text{CH}_2\text{CH}_2\text{O})_q\text{CH}_2\text{CH}_2\text{O}]$ and $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_q\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$ where q is from about 1 to about 100. If present, Each R_1 is independently selected from C_1 - C_4 alkyl, C_7 - C_{12} alkylaryl, or A. R_1 may be absent on some nitrogens; however, at least three nitrogens must be quaternized.

A is of the formula:



where R_3 is selected from H or C_1 - C_3 alkyl, n is from about 5 to about 100 and B is selected from H, C_1 - C_4 alkyl, acetyl, or benzoyl; m is from about 0 to about 4, and X is a water soluble anion.

In preferred embodiments, R is selected from C₄ to C₈ alkylene, R₁ is selected from C₁-C₂ alkyl or C₂-C₃ hydroxyalkyl, and A is:



where R₃ is selected from H or methyl, and n is from about 10 to about 50; and m is 1.

In another preferred embodiment R is linear or branched C₆, R₁ is methyl, R₃ is H, and n is from about 20 to about 50, and m is 1.

The levels of these polyethoxylated-polyamine polymers used can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight. These polyethoxylated-polyamine polymers can be synthesized following the methods outline in U.S. Patent No. 4,664,848, or other ways known to those skilled in the art.

Anionic Surfactant - The anionic surfactant system comprises surfactants selected from the group consisting of linear alkyl benzene sulphonates, alkyl sulfates, alkyl polyethoxylate sulfates and mixtures thereof. The detergent compositions of the present invention may contain other non-soap anionic surfactants, and are preferably essentially free of non-anionic surfactants.

Generally speaking, anionic surfactants useful herein are disclosed in U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981, and in U.S. Patent No. 3,919,678, Laughlin et al, issued December 30, 1975, both incorporated herein by reference.

Useful anionic surfactants include the water-soluble salts, particularly the alkali metal, ammonium and alkylolammonium (e.g., monoethanolammonium or triethanolammonium) salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of aryl groups.) Examples of this group of synthetic surfactants are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil.

Other anionic surfactants herein are the water-soluble salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 4 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group.

Other useful anionic surfactants herein include the water-soluble salts of esters of α-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and

from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and β -alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

The alkyl polyethoxylate sulfates usefule herein are of the formula $RO(C_2H_4O)_xSO_3^-M^+$ wherein R is an alkyl chain having from about 10 to about 22 carbon atoms, saturated or unsaturated, M is a cation which makes the compound water-soluble, especially an alkali metal, ammonium or substituted ammonium cation, and x averages from about 0.5 to about 15.

Preferred alkyl sulfate surfactants are the non-ethoxylated C₁₂₋₁₅ primary and secondary alkyl sulfates. Under cold water washing conditions, i.e., less than abut 65°F (18.3°C), it is preferred that there be a mixture of such ethoxylated and non-ethoxylated alkyl sulfates.

Fatty Acids - Moreover, the anionic surfactant component herein comprises fatty acids. These include saturated and/or unsaturated fatty acids obtained from natural sources or synthetically prepared. Examples of fatty acids include capric, lauric, myristic, palmitic, stearic, arachidic, and behenic acid. Other fatty acids include palmitoleic, oleic, linoleic, linolenic, and ricinolic acid.

Nonionic Detergent Surfactants - Suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, and U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981. Exemplary, non-limiting classes of useful nonionic surfactants include: C₈-C₁₈ alkyl ethoxylates ("AE"), with EO about 1-22, including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), alkyl dialkyl amine oxide, alkanoyl glucose amide, and mixtures thereof.

If nonionic surfactants are used, the compositions of the present invention will preferably contain up to about 10%, preferably from 0% to about 5%, more preferably from 0% to about 3%, by weight of an nonionic surfactant. Preferred are the ethoxylated alcohols and ethoxylated alkyl phenols of the formula $R(OC_2H_4)_nOH$, wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to

about 12 carbon atoms, and the average value of n is from about 5 to about 15. These surfactants are more fully described in U.S. Patent No. 4,284,532, Leikhim et al, issued August 18, 1981. Particularly preferred are ethoxylated alcohols having an average of from about 10 to about 15 carbon atoms in the alcohol and an average degree of ethoxylation of from about 6 to about 12 moles of ethylene oxide per mole of alcohol.

Other nonionic surfactants for use herein include:

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal[®] CO-630, marketed by the GAF Corporation; and Triton[®] X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company. These compounds are commonly referred to as alkyl phenol alkoxylates, (e.g., alkyl phenol ethoxylates).

The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 10 to about 20 carbon atoms with from about 2 to about 18 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol[®] 15-S-9 (the condensation product of C₁₁-C₁₅ linear secondary alcohol with 9 moles ethylene oxide), Tergitol[®] 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol[®] 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), Neodol[®] 23-6.5 (the condensation product of C₁₂-C₁₃ linear alcohol with 6.5 moles of ethylene oxide), Neodol[®] 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), Neodol[®] 45-4 (the condensation product of C₁₄-C₁₅ linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kryo[®] EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company. Other commercially available nonionic surfactants include Dobanol 91-8[®]

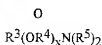
marketed by Shell Chemical Co. and Genapol UD-080[®] marketed by Hoechst. This category of nonionic surfactant is referred to generally as "alkyl ethoxylates."

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic[®] surfactants, marketed by BASF.

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetric[®] compounds, marketed by BASF.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



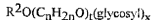
wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10} - C_{18} alkyl dimethyl amine oxides and C_8 - C_{12} alkoxyethyl dihydroxyethyl amine oxides.

Alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

Optionally, and less desirably, there can be a polyalkylene-oxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyl, dodecyl, undecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-sides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-sides and tallow alkyl tetra-, penta-, and hexa-glucosides.

The preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly the 2-position.

Fatty acid amide surfactants having the formula:



wherein R^6 is an alkyl group containing from about 7 to about 21 (preferably from about 9 to about 17) carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, and $-(C^2H_4O)_xH$ where x varies from about 1 to about 3.

Preferred amides are C_8 - C_{20} ammonia amides, monoethanolamides, diethanolamides, and isopropanolamides.

Cationic/amphoteric - Non-quaternary, cationic detergent surfactants can also be included in detergent compositions of the present invention. Cationic surfactants useful herein are described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980.

Ampholytic surfactants can be incorporated into the detergent compositions hereof. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35 for examples of ampholytic surfactants. Preferred amphoteric include C_{12} - C_{18} alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C_6 - C_{12} alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C_{12} - C_{18} betaines and sulfobetaines ("sultaines"), C_{10} - C_{18} amine oxides, and mixtures thereof.

Polyhydroxy Fatty Acid Amide Surfactant - The detergent compositions hereof may also contain polyhydroxy fatty acid amide surfactant. The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:



wherein: R^1 is H, C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C_1 - C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5 - C_{31} hydrocarbyl, preferably straight chain C_7 - C_{19} alkyl or alkenyl, more preferably straight chain C_9 - C_{17} alkyl or alkenyl, most preferably straight chain C_{11} - C_{15} alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxyated or propoxyated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glycidyl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$, $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$, and alkoxyated derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycidyls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$.

R' can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

$\text{R}^2\text{-CO-N}$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucyl, 2-deoxyfructyl, 1-deoxymaltyl, 1-deoxylactyl, 1-deoxygalactyl, 1-deoxymannyl, 1-deoxymaltotriitolyl, etc.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making

compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

Enzyme Stabilizing System - Enzyme-containing, including but not limited to, liquid compositions, herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition. See Severson, U.S. 4,537,706 for a review of Borate stabilizers.

Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired.

Enzymes - Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active bleach, detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as dishware and the like. In practical terms for current commercial preparations, the compositions herein may comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme

preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Other Enzymes - enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from surfaces such as textiles or dishes, for the prevention of refugee dye transfer, for example in laundering, and for fabric restoration. Suitable other enzymes include proteases, lipases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases.

"Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent composition.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may be desirable in highly concentrated detergent formulations.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor

International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Amylase - Amylase enzymes include those described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056. These enzymes are incorporated into detergent compositions at a level from 0.00018% to 0.060% pure enzyme by weight of the total composition, more preferably from 0.00024% to 0.048% pure enzyme by weight of total weight composition.

Specific amylase enzymes for use in the detergent compositions of the present invention therefore include:

- (a) α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas[®] α -amylase activity assay. Such Phadebas[®] α -amylase activity assay is described at pages 9-10, WO95/26397.
- (b) α -amylases according (a) comprising the amino sequence shown in the SEQ ID listings in the above cited reference, or an α -amylase being at least 80% homologous with the amino acid sequence shown in the SEQ ID listing.
- (c) α -amylases according (a) comprising the following amino sequence in the N-terminal : His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp.

A polypeptide is considered to be X% homologous to the parent amylase if a comparison of the respective amino acid sequences, performed via algorithms, such as the one described by Lipman and Pearson in Science 227, 1985, p. 1435, reveals an identity of X%

- (d) α -amylases according (a-c) wherein the α -amylase is obtainable from an alkalophilic *Bacillus* species; and in particular, from any of the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935.

In the context of the present invention, the term "obtainable from" is intended not only to indicate an amylase produced by a Bacillus strain but also an amylase encoded by a DNA sequence isolated from such a Bacillus strain and produced in an host organism transformed with said DNA sequence.

(e) α -amylase showing positive immunological cross-reactivity with antibodies raised against an α -amylase having an amino acid sequence corresponding respectively to those α -amylases in (a-d).

(f) Variants of the following parent α -amylases which (i) have one of the amino acid sequences shown in corresponding respectively to those α -amylases in (a-e), or (ii) displays at least 80% homology with one or more of said amino acid sequences, and/or displays immunological cross-reactivity with an antibody raised against an α -amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence which hybridizes with the same probe as a DNA sequence encoding an α -amylase having one of said amino acid sequence; in which variants :

1. at least one amino acid residue of said parent α -amylase has been deleted; and/or
 2. at least one amino acid residue of said parent α -amylase has been replaced by a different amino acid residue; and/or
 3. at least one amino acid residue has been inserted relative to said parent α -amylase;
- said variant having an α -amylase activity and exhibiting at least one of the following properties relative to said parent α -amylase : increased thermostability, increased stability towards oxidation, reduced Ca ion dependency, increased stability and/or α -amylolytic activity at neutral to relatively high pH values, increased α -amylolytic activity at relatively high temperature and increase or decrease of the isoelectric point (pI) so as to better match the pI value for α -amylase variant to the pH of the medium.

The preferred amylases of this invention are those described by the following:

- (a) α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadobas[®] α -amylase activity assay;
- (b) α -amylase showing positive immunological cross-reactivity with antibodies raised against an α -amylase having an amino acid sequence corresponding respectively to those α -amylases in (a); and
- (c) mixtures thereof.

Said variants are described in the patent application PCT/DK96/00056.

Other amylases suitable herein include, for example, α -amylases described in GB 1,296,839 to Novo; RAPIDASE[®], International Bio-Synthetics, Inc. and TERMAMYL[®], Novo. FUNGAMYL[®] from Novo is especially useful.

Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp. 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents, especially improved oxidative stability as measured against a reference-point of TERMAMYL[®] in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597.

Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* α -amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Such preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B. licheniformis* alpha-amylase, known as TERMAMYL[®], or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B. subtilis*, or *B. stearothermophilus*; (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B. licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with

the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®, (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Proteases - Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

In more detail, an especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al,

entitled "Protease-Containing Cleaning Compositions" having US Serial No. 08/322,676, and C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, both filed October 13, 1994.

Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303,761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein, Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985.

Also preferred proteases are subtilisin enzymes, in particular BPN', that have been modified by mutating the various nucleotide sequences that code for the enzyme, thereby modifying the amino acid sequence of the enzyme. These modified subtilisin enzymes have decreased adsorption to and increased hydrolysis of an insoluble substrate as compared to the wild-type subtilisin. Also suitable are mutant genes encoding for such BPN' variants.

Preferred BPN' variants comprise wild-type amino acid sequence wherein the wild-type amino acid sequence at one or more of positions 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 218, 219 or 220 is substituted; wherein the BPN' variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin BPN'. Preferably, the positions having a substituted amino acid are 199, 200, 201, 202, 205, 207, 208, 209, 210, 211, 212, or 215; more preferably, 200, 201, 202, 205 or 207.

Preferred protease enzymes for use according to the present invention also include the subtilisin 309 variants. These protease enzymes include several classes of subtilisin 309 variants.

A. Loop Region 6 Substitution Variants - These subtilisin 309 variants have a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the modified amino acid sequence comprises a substitution at one or more of positions 193, 194, 195, 196, 197, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213 or 214; whereby the subtilisin 309 variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309. Preferably these proteases have amino acids substituted at 193, 194, 195, 196, 199, 201, 202, 203, 204, 205, 206 or 209; more preferably 194, 195, 196, 199 or 200.

B. Multi-Loop Regions Substitution Variants - These subtilisin 309 variants may also be a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the modified amino acid sequence comprises a substitution at one or more positions in one or more of the first, second, third, fourth, or fifth loop regions; whereby the subtilisin 309 variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309.

C. Substitutions at positions other than the loop regions - In addition, one or more substitution of wild-type subtilisin 309 may be made at positions other than positions in the loop regions, for example, at position 74. If the additional substitution to the subtilisin 309 is mad at position 74 alone, the substitution is preferably with Asn, Asp, Glu, Gly, His, Lys, Phe or Pro, preferably His or Asp. However modifications can be made to one or more loop positions as well as position 74, for example residues 97, 99, 101, 102, 105 and 121.

Subtilisin BPN' variants and subtilisin 309 variants are further described in WO 95/29979, WO 95/30010 and WO 95/30011, all of which were published November 9, 1995, all of which are incorporated herein by reference.

Lipases - Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19,154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. Other suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Further suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades). Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE[®] enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Highly preferred lipases are the D96L lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in US Serial No. 08/341,826. (See also patent application WO 92/05249 viz. wherein the native lipase ex *Humicola lanuginosa*

aspartic acid (D) residue at position 96 is changed to Leucine (L). According to this nomenclature said substitution of aspartic acid to Leucine in position 96 is shown as : D96L.) Preferably the *Humicola lanuginosa* strain DSM 4106 is used.

In spite of the large number of publications on lipase enzymes, only the lipase derived from *Humicola lanuginosa* and produced in *Aspergillus oryzae* as host has so far found widespread application as additive for fabric washing products. It is available from Novo Nordisk under the tradename Lipolase™, as noted above. In order to optimize the stain removal performance of Lipolase, Novo Nordisk have made a number of variants. As described in WO 92/05249, the D96L variant of the native *Humicola lanuginosa* lipase improves the lard stain removal efficiency by a factor 4.4 over the wild-type lipase (enzymes compared in an amount ranging from 0.075 to 2.5 mg protein per liter). Research Disclosure No. 35944 published on March 10, 1994, by Novo Nordisk discloses that the lipase variant (D96L) may be added in an amount corresponding to 0.001-100- mg (5-500,000 LU/liter) lipase variant per liter of wash liquor.

Lipase enzyme is incorporated into the composition in accordance with the invention at a level of from 50 LU to 8500 LU per liter wash solution. Preferably the variant D96L is present at a level of from 100 LU to 7500 LU per liter of wash solution. More preferably at a level of from 150 LU to 5000 LU per liter of wash solution.

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

Cellulase Enzymes - The laundry detergent compositions according to the present invention may further comprise at least 0.001% by weight, preferably at least about 0.01%, of a cellulase enzyme. However, an effective amount of cellulase enzyme is sufficient for use in the laundry detergent compositions described herein. The term "an effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. The compositions herein will typically comprise from about 0.05% to about 2%, preferably from about 0.1% to about 1.5% by weight of a commercial enzyme preparation. The cellulase enzymes of the present invention are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per

gram of composition. Preferably, the optimum pH of the enzyme-containing composition is between about 7 and about 9.5.

U. S. Patent No. 4,435,307, Barbesgaard et al, issued March 6, 1984, discloses cellulase produced from *Humicola insolens*. Examples of other suitable cellulases include those produced by a strain of *Humicola insolens*, *Humicola grisea* var. *thermoidea*, and cellulases produced by a species of *Bacillus* sp. or *Aeromonas* sp. Other useful cellulases are those extracted from the hepatopancreas of the marine mollusc *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in the following: GB 2,075,028 A (Novo Industri A/S); GB 2,095,275 A (Kao Soap Co., Ltd.); and Horikoshi et al, U.S. Patent No. 3,844,890 (Rikagaku Kenkyusho). In addition, suitable cellulases and methods for their preparation are described in PCT International Publication Number WO 91/17243, published November 14, 1991, by Novo Nordisk A/S.

Cellulases are known in the art and can be obtained from suppliers under the tradenames: Celluzyme®, Endolase®, and Carezyme®.

For industrial production of the cellulases herein it is preferred that recombinant DNA techniques be employed. However other techniques involving adjustments of fermentations or mutation of the microorganisms involved can be employed to ensure overproduction of the desired enzymatic activities. Such methods and techniques are known in the art and may readily be carried out by persons skilled in the art.

Perfumes - Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 4%, by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Material Care Agents - The present compositions may optionally contain as corrosion inhibitors and/or anti-tarnish aids one or more material care agents such as silicates. Material care agents include bismuth salts, transition metal salts such as those of manganese, certain types of paraffin, triazoles, pyrazoles, thiols, mercaptans, aluminium fatty acid salts, and mixtures thereof and are preferably incorporated at low levels, e.g., from about 0.01% to

about 5% of the composition. A preferred paraffin oil is a predominantly branched aliphatic hydrocarbon comprising from about 20 to about 50 carbon atoms with a ratio of cyclic to noncyclic hydrocarbons of about 32 to 68 sold by Wintershall, Salzbergen, Germany as WINOG 70®. $\text{Bi}(\text{NO}_3)_3$ may be added. Other corrosion inhibitors are illustrated by benzotriazole, thiols including thionaphthol and thioanthranol, and finely divided aluminium fatty acid salts. All such materials will generally be used judiciously so as to avoid producing spots or films on glassware or compromising the bleaching action of the compositions. For this reason, it may be preferred to formulate without mercaptan anti-tarnishes which are quite strongly bleach-reactive or common fatty carboxylic acids which precipitate with calcium.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Other polymeric materials which can be included are polypropylene glycol (PPG), propylene glycol (PG), and polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Alkoxyated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxyated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

The levels of these dispersants used can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight. These dispersants can be synthesized

following the methods outline in US. Patent No. 4,664,848, or other ways known to those skilled in the art.

Dye Fixative Materials - optionally but preferred for use herein are selected dye fixative materials which do not form precipitates with anionic surfactant.

The selected dye fixatives useful herein may be in the form of unpolymerized materials, oligomers or polymers. Moreover, the preferred dye fixatives useful herein are cationic. The dye fixative component of the compositions herein will generally comprise from about 0.1% to 5% by the weight of the composition. More preferably, such dye fixative materials will comprise from about 0.5% to 4% by weight of the compositions, most preferably from about 1% to 3%. Such concentrations should be sufficient to provide from about 10 to 100 ppm of the dye fixative in the aqueous washing solutions formed from the laundry detergent compositions herein. More preferably from about 20 to 60 ppm of the dye fixative will be delivered to the aqueous washing solution, most preferably about 50 ppm.

The non-precipitating dye fixatives useful herein include a number that are commercially marketed by CLARIANT Corporation under the Sandofix[®], Sandolec[®] and Polymer VRN[®] tradenames. These include, for example, Sandofix SWE[®], Sandofix WA[®], Sandolec CT[®], Sandolec CS[®], Sandolec CI[®], Sandolec CF[®], Sandolec WA[®] and Polymer VRN[®]. Other suitable dye fixatives are marketed by Ciba-Geigy Corporation under the tradename Cassofix FRN-300[®] and by Hoechst Celanese Corporation under the tradename Tinofix EW[®].

Builders - Detergent builders can optionally but preferably be included in the compositions herein, for example to assist in controlling mineral, especially Ca and/or Mg, hardness in wash water or to assist in the removal of particulate soils from surfaces. Builder level can vary widely depending upon end use and physical form of the composition. Built detergents typically comprise at least about 1% builder. Liquid formulations typically comprise about 5% to about 50%, more typically 5% to 35% of builder. Lower or higher levels of builders are not excluded. For example, certain detergent additive or high-surfactant formulations can be unbuilt.

Suitable builders herein can be selected from the group consisting of phosphates and polyphosphates, especially the sodium salts; silicates including water-soluble and hydrous solid types and including those having chain-, layer-, or three-dimensional- structure as well as amorphous-solid or non-structured-liquid types; carbonates, bicarbonates, sesquicarbonates and carbonate minerals other than sodium carbonate or sesquicarbonate;

aluminosilicates; organic mono-, di-, tri-, and tetracarboxylates especially water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylates including aliphatic and aromatic types; and phytic acid.

Builder mixtures, sometimes termed "builder systems" can be used and typically comprise two or more conventional builders, optionally complemented by chelants, pH-buffers or fillers, though these latter materials are generally accounted for separately when describing quantities of materials herein.

P-containing detergent builders often preferred where permitted by legislation include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates exemplified by the triphosphates, pyrophosphates, glassy polymeric meta-phosphates; and phosphonates.

Suitable silicate builders include alkali metal silicates, particularly those liquids and solids having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1, including, particularly for automatic dishwashing purposes, solid hydrous 2-ratio silicates marketed by PQ Corp. under the tradename BRITESIL[®], e.g., BRITESIL H₂O; and layered silicates, e.g., those described in U.S. 4,664,839, May 12, 1987, H. P. Rieck. See preparative methods in German DE-A-3,417,649 and DE-A-3,742,043.

Also suitable for use herein are synthesized crystalline ion exchange materials or hydrates thereof as taught in U.S. 5,427,711, Sakaguchi et al, June 27, 1995.

Suitable carbonate builders include alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are especially useful in granular detergents, but can also be incorporated in liquids. Suitable for the present purposes are those having empirical formula: $[\text{M}_x(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and v are integers of at least 6, the molar ratio of z to v is in the range from 1.0 to 0.5, and x is an integer from 15 to 264. Aluminosilicates can be crystalline or amorphous, naturally-occurring or synthetically derived. An aluminosilicate production method is in U.S. 3,985,669, Krummel, et al, October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials are available as Zeolite A, Zeolite P (B), Zeolite X and, to whatever extent this differs from Zeolite P, the so-called Zeolite MAP.

Suitable organic detergent builders include polycarboxylate compounds, including water-soluble nonsurfactant dicarboxylates and tricarboxylates. More typically builder polycarboxylates have a plurality of carboxylate groups, preferably at least 3 carboxylates.

Carboxylate builders can be formulated in acid, partially neutral, neutral or overbased form. When in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. Polycarboxylate builders include the ether polycarboxylates, such as oxydisuccinate, see Berg, U.S. 3,128,287, April 7, 1964, and Lamberti et al, U.S. 3,635,830, January 18, 1972; "TMS/TDS" builders of U.S. 4,663,071, Bush et al, May 5, 1987; and other ether carboxylates including cyclic and alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other suitable builders are the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether; 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid; carboxymethyloxysuccinic acid; the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid; as well as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Oxydisuccinates are also especially useful in such compositions and combinations.

Certain deterative surfactants or their short-chain homologs also have a builder action. For unambiguous formula accounting purposes, when they have surfactant capability, these materials are summed up as deterative surfactants. Preferred types for builder functionality are illustrated by: 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984, Bush, January 28, 1986. Succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. Succinate builders also include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Lauryl-succinates are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986. Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions as surfactant/builder materials alone or in combination with the aforementioned builders, especially citrate and/or the succinate builders, to provide additional builder activity. Other suitable polycarboxylates are disclosed in U.S. 4,144,226, Crutchfield et al, March 13, 1979 and in U.S. 3,308,067, Dichl, March 7, 1967. See also Dichl, U.S. 3,723,322.

Other types of inorganic builder materials which can be used have the formula (M_x)_iCa_y(CO₃)_z wherein x and i are integers from 1 to 15, y is an integer from 1 to 10, z is an integer from 2 to 25, M_i are cations, at least one of which is a water-soluble, and the equation $\Sigma_i = 1.15(x_i \text{ multiplied by the valence of } M_i) + 2y = 2z$ is satisfied such that the

formula has a neutral or "balanced" charge. These builders are referred to herein as "Mineral Builders".

Polymeric Soil Release Agent - Known polymeric soil release agents, hereinafter "SRA" or "SRA's", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the composition.

SRA's can include a variety of charged, e.g., anionic or even cationic (see U.S. 4,956,447), as well as noncharged monomer units and structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. See U.S. 4,711,730, December 8, 1987 to Gosselink et al, for examples of those produced by transesterification/ oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, Me-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al.

SRA's also include simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; and the C₁-C₄ alkylcelluloses and C₄ hydroxyalkyl celluloses; see U.S. 4,000,093, December 28, 1976 to Nicol, et al. Suitable SRA's characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate), grafted onto polyalkylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially

available examples include SOKALAN SRA's such as SOKALAN HP-22, available from BASF, Germany. Other SRA's are polyesters with repeat units containing 10-15% by weight of ethylene terephthalate together with 90-80% by weight of polyoxyethylene terephthalate, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Commercial examples include ZELCON 5126 from Dupont and MILEASE T from ICI.

U.S. 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995. Suitable monomers for the above SRA include Na 2-(2-hydroxyethoxy)-ethanesulfonate, DMT, N-dimethyl 5-sulfoisophthalate, EG and PG.

Additional classes of SRA's include (I) nonionic terephthalates using diisocyanate coupling agents to link up polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al; (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With a proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.; (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al; (IV) poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate, including both nonionic and cationic polymers, see U.S. 4,579,681, Ruppert et al.; (V) graft copolymers, in addition to the SOKALAN types from BASF made, by grafting acrylic monomers on to sulfonated polyesters; these SRA's assertedly have soil release and anti-redeposition activity similar to known cellulose ethers: see EP 279,134 A, 1988, to Rhone-Poulenc Chemie; (VI) grafts of vinyl monomers such as acrylic acid and vinyl acetate on to proteins such as caseins, see EP 457,205 A to BASF (1991); (VII) polyester-polyamide SRA's prepared by condensing adipic acid, caprolactam, and polyethylene glycol, especially for treating polyamide fabrics, see Bevan et al, DE 2,335,044 to Unilever N. V., 1974. Other useful SRA's are described in U.S. Patents 4,240,918, 4,787,989, 4,525,524 and 4,877,896.

Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.01% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid,

methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artie White CC and Artie White CWD, the 2-(4-styryl-phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)biphenyls; and the aminocoumarins. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.

Dye Transfer Inhibiting Agents - The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

The N-O group can be represented by the following general structures:

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a poly-vinyl-pyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

Particular brightener species, commercially marketed under the tradenames Tinopal-UNPA-GX, Tinopal AMS-GX, and Tinopal 5BM-GX by Ciba-Geigy Corporation, are also included. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

Suds Suppressors - Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as

products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethyl-siloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

Alkoxyated Polycarboxylates - Alkoxyated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked

to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

The compositions of this invention can be used to form aqueous washing solutions for use in the laundering of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine, to form such aqueous laundering solutions. The aqueous washing solution so formed is then contacted, preferably under agitation, with the fabrics to be laundered therewith.

An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering solutions can comprise amounts sufficient to form from about 500 to 7,000 ppm of composition in aqueous solution. More preferably, from about 800 to 3,000 ppm of the detergent compositions herein will be provided in aqueous washing solution.

EXAMPLES

The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

In the following Examples all levels are quoted as % by weight of the composition.

EXAMPLE I

The following non-limiting examples are within the scope of the present invention.

Table I

Example	4	5	6	7
C12-15E2.5S		23.50		
C12-15E1.8S	23.50		23.50	23.50
C12LAS	3.00	3.00		
C12-14 glucosamide			3.00	3.00
C12-15EO7		2.00		
C12-13EO9	2.00		2.00	2.00
C10 amidopropylamine	1.50	1.50	1.50	1.50
citric acid	2.50	2.50	2.50	2.50
DTPA	0.50		0.50	0.50
DTPMP		1.00		
polyacrylate				
polyaspartate				
C12-16 fatty acid	5.00	5.00	5.00	9.00
rapeseed fatty acid	6.50	6.50	6.50	
oleic acid				3.00
protease	0.88	0.88	0.88	0.88
amylase	0.10	0.10	0.10	0.10
cellulase	0.05	0.05	0.05	0.05
brightener	0.15	0.15	0.15	0.15
polymer A	1.20	1.20	1.20	1.20
ethanol	0.50	0.50	0.50	0.50
1,2-propanediol	4.00	4.00	4.00	4.00
MEA	0.48	0.48	0.48	0.48
NaOH	7.00	7.00	7.00	7.00
Na2SO4	1.75	0.50	1.75	1.75
borax	2.50	2.50	2.50	2.50
suds supressor	0.06	0.06	0.06	0.06
perfume	0.50	0.50	0.50	0.50
dye	0.02	0.02	0.02	0.02
water	bal.	bal.	bal.	Bal.

Table 1, continued

Example	8	9	10	11
C12-15E2.5S				
C12-15E1.8S	23.50	23.50	23.50	23.50
C12LAS	3.00	3.00	3.00	3.00
C12-14 glucosamide				
C12-15EO7				
C12-13EO9	2.00	2.00	2.00	2.00
C10 amidopropylamine		1.50	1.50	1.50
citric acid	2.50	2.50	1.50	1.50
DTPA	0.50	0.50	0.50	0.50
DTPMP				
polyacrylate			1.50	
polyaspartate				1.50
C12-16 fatty acid	5.00	5.00	5.00	5.00
rapeseed fatty acid	6.50	6.50	6.50	6.50
oleic acid				
protease	0.88	0.88	0.88	0.88
amylase	0.10	0.10	0.10	0.10
cellulase	0.05	0.05	0.05	0.05
brightener	0.15	0.15	0.15	0.15
polymer A	1.20			
ethanol	0.50	0.50	0.50	0.50
1,2-propanediol	4.00	4.00	4.00	4.00
MEA	0.48	0.48	0.48	0.48
NaOH	7.00	7.00	7.00	7.00
Na ₂ SO ₄	1.75	1.75	1.25	1.25
borax	2.50	2.50	2.50	2.50
suds supressor	0.06	0.06	0.06	0.06
perfume	0.50	0.50	0.50	0.50
dye	0.02	0.02	0.02	0.02
water	bal.	bal.	bal.	bal.

Polymer A = tetrachylenepentaamine with an average degree of ethoxylation of 15

Monothanolamine = (MEA)

Quaternary Surfactant is selected from one or more of the following: lauryl trimethyl ammonium chloride, myristyl trimethyl ammonium chloride, palmityl trimethyl ammonium chloride, coconut trimethylammonium chloride, coconut trimethylammonium methylsulfate, coconut dimethyl-monohydroxyethyl-ammonium chloride, coconut dimethyl-monohydroxyethylammonium methylsulfate, steryl dimethyl-monohydroxy-ethylammonium chloride, steryl dimethylmonohydroxy-ethylammonium methylsulfate, di-C₁₂-C₁₄ alkyl dimethyl ammonium chloride.

The polyamide-polyamines herein are commercially marketed under the tradenames: Kymene

®, Kymene 557H®, Kymene 557LX®, Reten®, and Cartaretin®.

What is claimed is:

1. A gel laundry detergent composition characterized by, by weight of the composition:
 - a) from 10% to 40%, preferably from 2.0% to 6.0%, by weight of the composition, of an anionic surfactant system:
 - b) from 5% to 20%, by weight of the composition, of fatty acids; and
 - c) and from 0.5% to 6%, preferably from 1.0% to 5.0%, of a structurant characterized by sodium sulfate.
2. A composition according to Claim 1 wherein the anionic surfactant system comprises from 5% to 25%, by weight of the composition, of alkyl polyethoxylate sulfates wherein the alkyl group contains from 10 to 22 carbon atoms and the polyethoxylate chain contains from 0.5 to 15 ethylene oxide moieties.
3. A composition according to Claim 1 wherein the detergent composition additionally comprises adjunct ingredients selected from the group consisting of non-citrate builders, optical brighteners, soil release polymers, dye transfer inhibitors, polymeric dispersing agents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, antiredeposition agents, antifading agent, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof.
4. A composition according to Claim 1 wherein the detergent composition additionally comprises one or more amine containing detergent materials selected from the group consisting of detergent amines, modified polyamines, polyamide-polyamines, polyethoxylated-polyamine polymers, quaternary ammonium surfactants, and mixtures thereof.
5. A composition according to Claim 1 wherein the structurant further comprises a detergent builder selected from the group consisting of carboxylates, polycarboxylates, amino carboxylates, polycarboxylates, carbonates, bicarbonates, phosphates, phosphonates and mixtures thereof.
6. A composition according to Claim 1 wherein the anionic surfactant system comprises surfactants is selected from linear alkyl benzene sulfonate, alkyl sulfate, alkyl ethoxy sulfate and mixtures thereof.
7. A composition according to any of claims 1-6 wherein the detergent builder is citrate.

8. A composition according to any of claims 1-6 wherein the weight ratio of sodium sulfate to detergent builder is from 5:1 to 1:5, preferably from 3:1 to 1:3.
9. A composition according to any of claims 1-2 wherein the polyethoxylate chains of the alkyl polyethoxylate sulfates contain from 0.5 to 5 ethylene oxide moieties.
10. A composition according to Claim 1 wherein the sodium sulfate is present from 3.0% to 5.0%, by weight of the composition.

INTERNATIONAL SEARCH REPORT

 Internat: Application No
 PCT/US 98/24809

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D17/00 C11D3/02 C11D10/04 C11D1/29

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 43396 A (PPG INDUSTRIES) 20 November 1997 see page 2, line 18-21; claims 1,3,4	1
A	DATABASE WPI Week 8246 Derwent Publications Ltd., London, GB; AN 82-98238E XP002095979 & JP 57 162799 A (FUMAKILA) , 6 October 1982 see abstract	1,3
A	DE 37 17 600 A (HENKEL) 8 December 1988 see claims 1,2,6	1-3,6,9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
 "Z" document member of the same patent family

Date of the actual completion of the international search

9 March 1999

Date of mailing of the international search report

22/03/1999

Name and mailing address of the ISA

 European Patent Office, P.B. 5816 Patentlaan 2
 NL - 2200 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-2046

Authorized officer

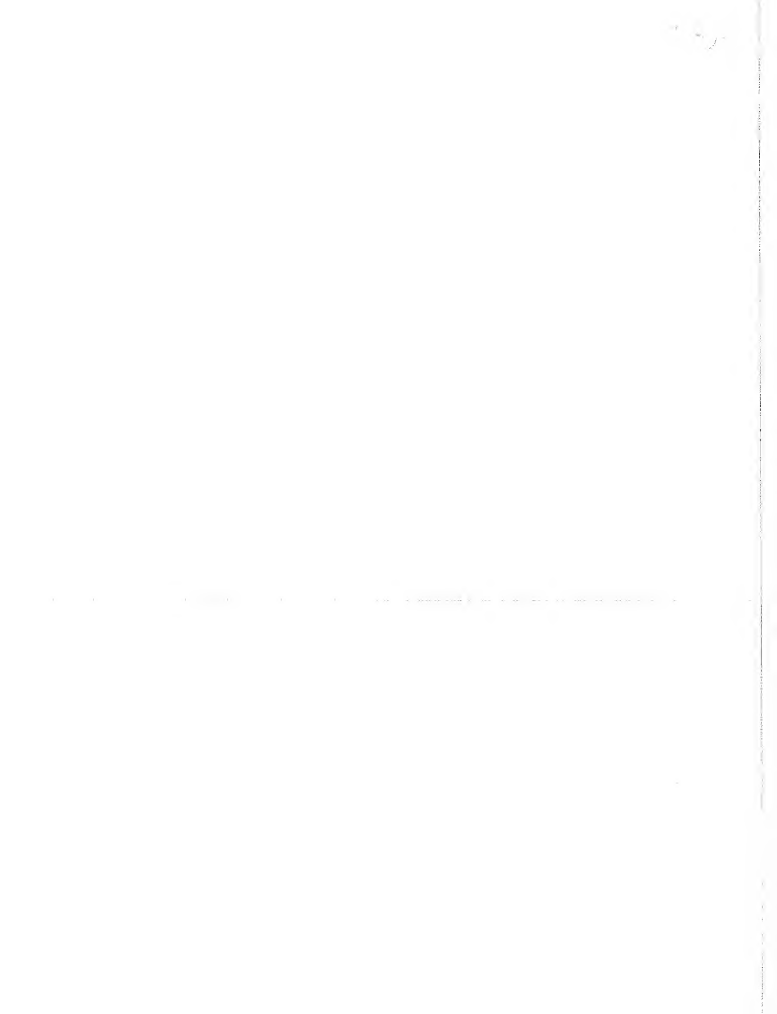
Van Bellingen, I

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No
PCT/US 98/24809

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9743396 A	20-11-1997	AU 3000997 A	05-12-1997
DE 3717600 A	08-12-1988	NONE	





INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C11D 3/37, 3/00	A1	(11) International Publication Number: WO 00/15747 (43) International Publication Date: 23 March 2000 (23.03.00)
--	----	---

(21) International Application Number: PCT/EP99/06429

(22) International Filing Date: 1 September 1999 (01.09.99)

(30) Priority Data:

9820205.2	16 September 1998 (16.09.98)	GB
9911474.6	17 May 1999 (17.05.99)	GB

(71) Applicant (for AE AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW only): UNILEVER PLC (GB/GB); Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for all designated States except AE AU BB CA CY GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW): UNILEVER N.V. (NL/NL); Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): HINDUSTAN LEVER LIMITED (IN/IN); Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN).

(72) Inventors: GRIFFITHS, Paula; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). HAQ, Ziya; 32 Latchford Road, Gayton, Wirral, Merseyside CH60 3RW (GB). JARVIS, Anthony, Nicholas; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). KRAVCHUK, Paul; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). PARKER, Andrew, Philip; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). SAMS, Philip, John; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). SHEN, Zhengwu; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).

(74) Agent: ELLIOTT, Peter, William; Unilever plc, Patent Dept., Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: FABRIC CARE COMPOSITION

(57) Abstract

Fabric care compositions comprising at least one amine- or amide-epichlorohydrin resin or derivative thereof and at least one textile compatible carrier, wherein the textile compatible carrier facilitates contact between the resin and a fabric, may be used in a laundering process to improve fabric dimensional stability of a fabric comprising cellulosic fibres. The fabric may contain cotton.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

FABRIC CARE COMPOSITION

Technical Field

- 5 This invention relates to fabric care compositions and, in particular, to the use of the fabric care compositions in a domestic laundering process to improve fabric dimensional stability.

Background and Prior Art

10

- The laundry process generally has several benefits for fabric, the most common being to remove dirt and stains from the fabric during the wash cycle and to soften the fabric during the rinse cycle. However, there are numerous disadvantages associated with repeated use of conventional laundry treatment
- 15 compositions and/or the actual laundry process; one of these being a fairly harsh treatment of fabric in the laundry process.

- Fabrics can be damaged in several ways as a result of repeated laundering and/or wear. Fabric pilling and loss of fabric surface appearance e.g. fuzzing, shrinkage
- 20 (or expansion), loss of colour from the fabric or running of colour on the fabric (usually termed dye transfer) are some of the common problems associated with repeated laundering. These problems may occur merely from repeated hand washing as well as the more vigorous machine washing process. Furthermore, problems relating to damage of fabric over time through normal use, such as loss
- 25 of shape and increased likelihood of wrinkling are also significant.

- 2 -

The present invention is directed towards alleviating one or more of the problems referred to hereinabove.

5 The principal advantage of the present invention relates to maintaining the dimensional stability of the fabric.

Laundry detergent compositions containing polyamide-polyamine fabric treatment agents are described in WO 98/29530. The compositions are claimed to impart improved overall appearance to fabrics laundered using the detergent
10 compositions, in terms of surface appearance properties such as pill/fuzz reduction and antifading. Laundry compositions containing polyamide-polyamine treatment agents of similar types are taught in WO 97/42287.

WO 96/15309 and WO 96/15310 describe anti-wrinkle compositions which
15 contain a silicone and a film-forming polymer. A wide range of possibilities is given for the film-forming polymer.

An industrial process for treating fibres is disclosed in US 3949014. This document describes the use of a polyamine-epichlorohydrin resin in a binder,
20 together with an amphoteric high molecular weight compound having at least 2 cationic groups and at least 2 anionic groups per molecule. US 3949014 mentions the treatment of fabrics with the binder but it is clear that the treatment is intended to be carried out industrially as part of a fabric treatment process rather than as part of a domestic laundering process and this conclusion is
25 supported by the fact that the fabric treated with the binder required curing at a

- 3 -

relatively high temperature. Industrial curing of fabrics treated with this type of polymer system is normally carried out at about 150°C.

Methods for treating wool with compositions containing an amino functional
5 polymer and a silicone polymer so as to impart shrink resistance are known.
However, as described in EP-A-0315477, wool requires a pretreatment before
such compositions can be used. Furthermore, EP-A-0372782 explains that the
chemistry of wool is quite different from that of cellulosic fibres such as cotton
and the requirements for shrink resistance treatments for cotton are generally very
10 different from those for wool.

US 4371517 discloses compositions for treating fibrous materials which contain
cationic and anionic polymers. In a non-domestic treatment, the compositions
increased the rigidity of cotton fabric.
15

Co-emulsifiers, for use in fabric softener and other compositions, which contain
cationic quaternary amine polymers, are taught in DD 221922.

The present invention is based on the surprising finding of a method for
20 alleviating the dimensional instability (eg shrinkage) of fabrics which comprise
cellulosic fibres such as cotton, for example. The term "dimensional stability",
and related terms, used herein covers not only shrinkage of fabrics but also shape
retention, bagginess reduction and additionally, although less preferred,
crease/wrinkle resistance in fabrics.

25

Definition of the Invention

- According to the present invention, there is provided the use of a fabric care composition comprising at least one amine- or amide-epichlorohydrin resin or derivative thereof and at least one textile compatible carrier, wherein the textile compatible carrier facilitates contact between the resin and a fabric, in a laundering process to improve fabric dimensional stability of a fabric comprising cellulosic fibres.
- 10 The invention also provides a method of treating fabric to improve its dimensional stability comprising applying to the fabric a composition comprising at least one amine- or amide-epichlorohydrin resin or derivative thereof and a textile compatible carrier, wherein the textile compatible carrier facilitates contact between the resin and the fabric, as part of a laundering process.

15

Detailed Description of the Invention

- The compositions of the present invention comprise, as the first component, at least one amine- or amide- epichlorohydrin resin or derivatives thereof.
- 20 In the context of the present invention these first materials are polymeric, or at least oligomeric, in nature. Preferably, they have a weight average mean molecular weight of from 300 to 1,000,000 daltons.
- 25 The resins of the invention are sometimes referred to below as amine-epichlorohydrin resins and polyamine-epichlorohydrin (PAE) resins (the two

- 5 -

terms being used synonymously) although these terms encompass both the amine and amide resins of the invention. The resins may also have a mixture of amine and amide groups.

- 5 The amine or amide-epichlorohydrin resins may have one or more functional groups capable of forming azetidinium groups and/or one or more azetidinium functional groups.



- Alternatively, or additionally the resins may have one or more functional groups
10 that contain epoxide groups or derivatives thereof e.g. Kymene 450™ (ex Hercules).

- Suitable polyamine-epichlorohydrin (PAE) resins include those described in 'Wet
Strength Resins and Their Application', pp 16-36, ed. L.L.Chan, Tappi Press,
15 Atlanta, 1994. Suitable PAE resins can be identified by selecting those resins
which impart increased wet strength to paper, after treatment, in a relatively
simple test.

- Any amine or amide-epichlorohydrin resin having an epoxide functional group or
20 derivative thereof is suitable for use according to the invention.

A particularly preferred class of amine or amide-epichlorohydrin resins for use in
the invention are secondary amine or amide-based azetidinium resins, for

- 6 -

example, those resins derived from a polyalkylene polyamine e.g. diethylenetriamine (DETA), a polycarboxylic acid e.g. adipic acid or other dicarboxylic acids, and epichlorohydrin. Other polyamines or polyamides can also be advantageously used in the preparation of suitable PAE resins.

5

Another preferred class of amine-epichlorohydrin resins for use in the invention are those having an epoxide functional group or derivative thereof e.g. chlorohydrin.

- 10 The resin is preferably present in the product in a sufficient quantity to give an amount of 0.0005% to 5% by weight on the fabric based on the weight of the fabric, more preferably 0.001% to 2% by weight on fabric. The amount of the first component in the composition required to achieve the above % by weight on fabric will typically be in the range 0.01% to 35% by weight, preferably 0.1 to
- 15 13.5% by weight.

The resins may be PDAA-epichlorohydrin resins or PMDAA-epichlorohydrin resins. PDAA is poly(diallylamine) and PMDAA is poly(methyldiallyl(amine)).

- 20 The compositions of the invention, when applied to a fabric, can impart benefits to the fabric when uncured. However, they may be cured by a domestic curing step including ironing and/or domestic tumble drying, preferably tumble drying. The curing is preferably carried out at a temperature in the range of from 50 to 100°C, more preferably from 80 to 100°C.

25

- 7 -

The composition of the invention may further comprise a silicone component. It is preferred if the silicone component is a dimethylpolysiloxane with amino alkyl groups. It may be used in the context of the present invention as an emulsion in water.

5

It is preferred if the silicone component is present in a ratio of first component: silicone of from 1:1 to 30:1, preferably 1:1 to 20:1, more preferably 2:1 to 20:1 and most preferably 5:1 to 15:1.

- 10 In the context of the present invention the term "textile compatible carrier" is a component which can assist in the interaction of the first component with the fabric. The carrier can also provide benefits in addition to those provided by the first component e.g. softening, cleaning etc. The carrier may be a water or a detergent-active compound or a fabric softener or conditioning compound or other
- 15 suitable detergent or fabric treatment agent.

If the composition of the invention is to be used in a laundry process as part of a conventional fabric treatment product, such as a detergent composition, the textile-compatible carrier will typically be a detergent-active compound.

- 20 Whereas, if the fabric treatment product is a rinse conditioner, the textile-compatible carrier will be a fabric softening and/or conditioning compound.

If the composition of the invention is to be used before, or after, the laundry process it may be in the form of a spray or foaming product.

25

- 8 -

The fabrics which may be treated in the present invention comprise cellulosic fibres, preferably from 1% to 100% cellulosic fibres (more preferably 5% to 100% cellulosic fibres, most preferably 40% to 100%). When the fabric contains less than 100% cellulosic fibres, the balance comprises other fibres or blends of fibres suitable for use in garments such as polyester, for example. Preferably, the cellulosic fibres are of cotton or regenerated cellulose such as viscose.

The laundering processes of the present invention include the large scale and small scale (eg domestic) cleaning of fabrics. Preferably, the processes are domestic.

In the invention, the resin is preferably used to treat the fabric in the rinse cycle of a laundering process. The rinse cycle preferably follows the treatment of the fabric with a detergent composition.

15

Detergent Active Compounds

If the composition of the present invention is in the form of a detergent composition, the textile-compatible carrier may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent active compounds, and mixtures thereof.

Many suitable detergent active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred textile-compatible carriers that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

5 Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15} ; primary and secondary alkylsulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

10

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the $C_{10}-C_{15}$ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated
15 nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

Cationic surfactants that may be used include quaternary ammonium salts of the
20 general formula $R_1R_2R_3R_4N^+ X^-$ wherein the R groups are independently hydrocarbyl chains of C_1-C_{22} length, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a solubilising cation (for example, compounds in which R_1 is a C_8-C_{22} alkyl group, preferably a C_8-C_{10} or $C_{12}-C_{14}$ alkyl group, R_2 is a methyl group, and R_3 and R_4 , which may be the same or different, are methyl or
25 hydroxyethyl groups); and cationic esters (for example, choline esters) and pyridinium salts.

- 10 -

The total quantity of detergent surfactant in the composition is suitably from 0.1 to 60 wt% e.g. 0.5-55 wt%, such as 5-50wt%.

- 5 Preferably, the quantity of anionic surfactant (when present) is in the range of from 1 to 50% by weight of the total composition. More preferably, the quantity of anionic surfactant is in the range of from 3 to 35% by weight, e.g. 5 to 30% by weight.
- 10 Preferably, the quantity of nonionic surfactant when present is in the range of from 2 to 25% by weight, more preferably from 5 to 20% by weight.

Amphoteric surfactants may also be used, for example amine oxides or betaines.

- 15 The compositions may suitably contain from 10 to 70%, preferably from 15 to 70% by weight, of detergency builder. Preferably, the quantity of builder is in the range of from 15 to 50% by weight.

- 20 The detergent composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate.

- 25 The aluminosilicate may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50%. Aluminosilicates are materials having the general formula:

- 11 -



where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO₂ units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

Fabric Softening and/or Conditioner Compounds

10

If the composition of the present invention is in the form of a fabric conditioner composition, the textile-compatible carrier will be a fabric softening and/or conditioning compound (hereinafter referred to as "fabric softening compound"), which may be a cationic or nonionic compound.

15

The softening and/or conditioning compounds may be water insoluble quaternary ammonium compounds. The compounds may be present in amounts of up to 8% by weight (based on the total amount of the composition) in which case the compositions are considered dilute, or at levels from 8% to about 50% by weight, in which case the compositions are considered concentrates.

20

Compositions suitable for delivery during the rinse cycle may also be delivered to the fabric in the tumble dryer if used in a suitable form. Thus, another product form is a composition (for example, a paste) suitable for coating onto, and delivery from, a substrate e.g. a flexible sheet or sponge or a suitable dispenser during a tumble dryer cycle.

25

- 12 -

Suitable cationic fabric softening compounds are substantially water-insoluble quaternary ammonium materials comprising a single alkyl or alkenyl long chain having an average chain length greater than or equal to C_{20} or, more preferably, compounds comprising a polar head group and two alkyl or alkenyl chains having an average chain length greater than or equal to C_{14} . Preferably the fabric softening compounds have two long chain alkyl or alkenyl chains each having an average chain length greater than or equal to C_{16} . Most preferably at least 50% of the long chain alkyl or alkenyl groups have a chain length of C_{18} or above. It is preferred if the long chain alkyl or alkenyl groups of the fabric softening compound are predominantly linear.

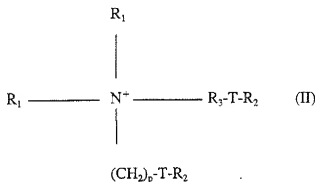
Quaternary ammonium compounds having two long-chain aliphatic groups, for example, distearyldimethyl ammonium chloride and di(hardened tallow alkyl) dimethyl ammonium chloride, are widely used in commercially available rinse conditioner compositions. Other examples of these cationic compounds are to be found in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. Any of the conventional types of such compounds may be used in the compositions of the present invention.

The fabric softening compounds are preferably compounds that provide excellent softening, and are characterised by a chain melting $L\beta$ to $L\alpha$ transition temperature greater than 25°C , preferably greater than 35°C , most preferably greater than 45°C . This $L\beta$ to $L\alpha$ transition can be measured by DSC as defined in "Handbook of Lipid Bilayers", D Marsh, CRC Press, Boca Raton, Florida, 1990 (pages 137 and 337).

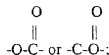
- 13 -

Substantially water-insoluble fabric softening compounds are defined as fabric softening compounds having a solubility of less than 1×10^{-3} wt % in demineralised water at 20°C. Preferably the fabric softening compounds have a solubility of less than 1×10^{-4} wt%, more preferably less than 1×10^{-8} to 1×10^{-6} wt%.

Especially preferred are cationic fabric softening compounds that are water-insoluble quaternary ammonium materials having two C_{12-22} alkyl or alkenyl groups connected to the molecule via at least one ester link, preferably two ester links. An especially preferred ester-linked quaternary ammonium material can be represented by the formula II:



wherein each R_1 group is independently selected from C_{1-4} alkyl or hydroxyalkyl groups or C_{2-4} alkenyl groups; each R_2 group is independently selected from C_{8-28} alkyl or alkenyl groups; and wherein R_3 is a linear or branched alkylene group of 1 to 5 carbon atoms, T is



- 14 -

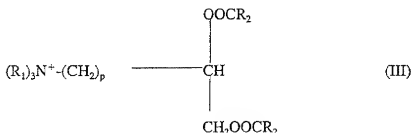
and p is 0 or is an integer from 1 to 5.

- 5 Di(tallowoxyloxyethyl) dimethyl ammonium chloride and/or its hardened tallow analogue is especially preferred of the compounds of formula (II).

A second preferred type of quaternary ammonium material can be represented by the formula (III):

10

15



wherein R_1 , p and R_2 are as defined above.

20

It is advantageous if the quaternary ammonium material is biologically biodegradable.

25

Preferred materials of this class such as 1,2-bis(hardened tallowoyloxy)-3-trimethylammonium propane chloride and their methods of preparation are, for example, described in US 4 137 180 (Lever Brothers Co). Preferably these materials comprise small amounts of the corresponding monoester as described in US 4 137 180, for example, 1-hardened tallowoyloxy-2-hydroxy-3-trimethylammonium propane chloride.

30

- 15 -

Other useful cationic softening agents are alkyl pyridinium salts and substituted imidazoline species. Also useful are primary, secondary and tertiary amines and the condensation products of fatty acids with alkyldiamines.

- 5 The compositions may alternatively or additionally contain water-soluble cationic fabric softeners, as described in GB 2 039 556B (Unilever).

The compositions may comprise a cationic fabric softening compound and an oil, for example as disclosed in EP-A-0829531.

10

The compositions may alternatively or additionally contain nonionic fabric softening agents such as lanolin and derivatives thereof.

Lecithins are also suitable softening compounds.

15

Nonionic softeners include L β phase forming sugar esters (as described in M Hato et al Langmuir 12, 1659, 1666, (1996)) and related materials such as glycerol monostearate or sorbitan esters. Often these materials are used in conjunction with cationic materials to assist deposition (see, for example, 20 GB 2 202 244). Silicones are used in a similar way as a co-softener with a cationic softener in rinse treatments (see, for example, GB 1 549 180).

25

The compositions may also suitably contain a nonionic stabilising agent. Suitable nonionic stabilising agents are linear C₈ to C₂₂ alcohols alkoxylated with 10 to 20 moles of alkylene oxide, C₁₀ to C₂₀ alcohols, or mixtures thereof. Advantageously the nonionic stabilising agent is a linear C₈ to C₂₂ alcohol alkoxylated with 10 to 20 moles of alkylene oxide. Preferably, the level of

- 16 -

- nonionic stabiliser is within the range from 0.1 to 10% by weight, more preferably from 0.5 to 5% by weight, most preferably from 1 to 4% by weight. The mole ratio of the quaternary ammonium compound and/or other cationic softening agent to the nonionic stabilising agent is suitably within the range from
- 5 40:1 to about 1:1, preferably within the range from 18:1 to about 3:1.

- The composition can also contain fatty acids, for example C_8 to C_{24} alkyl or alkenyl monocarboxylic acids or polymers thereof. Preferably saturated fatty acids are used, in particular, hardened tallow C_{16} to C_{18} fatty acids.
- 10 Preferably the fatty acid is non-saponified, more preferably the fatty acid is free, for example oleic acid, lauric acid or tallow fatty acid. The level of fatty acid material is preferably more than 0.1% by weight, more preferably more than 0.2% by weight. Concentrated compositions may comprise from 0.5 to 20% by weight of fatty acid, more preferably 1% to 10% by weight. The weight ratio of
- 15 quaternary ammonium material or other cationic softening agent to fatty acid material is preferably from 10:1 to 1:10.

- The fabric conditioning compositions may include silicones, such as predominately linear polydialkylsiloxanes, e.g. polydimethylsiloxanes or
- 20 aminosilicones containing amine-functionalised side chains; soil release polymers such as block copolymers of polyethylene oxide and terephthalate; amphoteric surfactants; smectite type inorganic clays; zwitterionic quaternary ammonium compounds; and nonionic surfactants.
- 25 The fabric conditioning compositions may also include an agent which produces a pearlescent appearance, e.g. an organic pearlising compound such as ethylene

- 17 -

glycol distearate, or inorganic pearlising pigments such as microfine mica or titanium dioxide (TiO₂) coated mica.

5 The fabric conditioning compositions may be in the form of emulsions or emulsion precursors thereof.

Other optional ingredients include emulsifiers, electrolytes (for example, sodium chloride or calcium chloride) preferably in the range from 0.01 to 5% by weight, pH buffering agents, and perfumes (preferably from 0.1 to 5% by weight).

10 Further optional ingredients include non-aqueous solvents, perfume carriers, fluorescers, colourants, hydrotropes, antifoaming agents, antiredeposition agents, enzymes, optical brightening agents, opacifiers, dye transfer inhibitors, anti-shrinking agents, anti-wrinkle agents, anti-spotting agents, germicides, 15 fungicides, anti-oxidants, UV absorbers (sunscreens), heavy metal sequestrants, chlorine scavengers, dye fixatives, anti-corrosion agents, drape imparting agents, antistatic agents and ironing aids. This list is not intended to be exhaustive.

Fabric Treatment Products

20 The composition of the invention may be in the form of a liquid, solid (e.g. powder or tablet), a gel or paste, spray, stick or a foam or mousse. Examples including a soaking product, a rinse treatment (e.g. conditioner or finisher) or a mainwash product. The composition may also be applied to a substrate e.g. a 25 flexible sheet or used in a dispenser which can be used in the wash cycle, rinse cycle or during the dryer cycle.

- 18 -

The invention will now be described by way of example only and with reference to the following non-limiting examples.

5

EXAMPLES

Experimental Procedure to show effect on dimensional stability

10 Experimental Procedure

The amine epichlorohydrin resin used in the following tests is Apomul SAK, (ex. Brookstone Chemicals) which has an azetidinium functional group. It was prepared as an aqueous solution and utilised as a percentage of the weight of fabric treated (% on weight of fabric (owf)) to show its effect on fabric dimensional stability.

15

Two types of fabric, cotton interlock and cotton poplin, were used in the procedure below. Each fabric was tested in the weft and warp direction, figures relating to the % dimensional change (by multiplying the % change in the weft direction by the % change in the warp direction) have been tabulated.

20

All fabrics pieces were pre-washed prior to treating (40°C cotton wash in a Miele Novotronic W820 Front Loading Washing Machine, Wirral water, 100g Persil non biological washing powder, then tumble dried in a Miele Novotronic T430 Tumble Dryer). The fabrics pieces were then marked up using the M&S Shrinkage Rule and labelled. Four pieces of each fabric type plus clean cotton sheeting made up a 2.5kg load, which was washed (40°C cotton wash in a Miele

25

- 19 -

- Novotronic W820 Front Loading Washing Machine, Wirral water, 100g Persil non biological washing powder added in the main wash. Apomul SAK was added in the final rinse), then tumble dried in a Miele Novotronic T430 Tumble Dryer, and finally lightly ironed on both sides (cotton setting). Ironing only took place
- 5 after the first wash. The fabric pieces were then conditioned for 24 hours at 65% RH, 20°C. The washing and drying stages were repeated until five washes were completed.

EXAMPLE 1

10

The % dimensional change results are given in the tables below. % dimensional change was calculated by multiplying the mean warp % values by the mean weft % values, i.e. the mean value is calculated from the values obtained before and after each test.

15

Dose Response - Tumble Drying

Cotton Interlock Fabric - % Dimensional Change

Wash Number	Water Control	SAK (0.054% owf)	SAK (0.135% owf)	SAK (0.27% owf)	SAK (0.54% owf)
1	1.97	13.51	7.49	1.21	7.49
2	12.10	4.04	2.90	3.40	1.73
3	13.83	5.58	2.83	5.65	1.80
4	29.28	5.67	0.77	7.15	0.21
5	24.36	12.46	8.71	12.27	3.89

- 20 -

Cotton Poplin Fabric - % Dimensional Change

Wash Number	Water Control	SAK (0.054 % owf)	SAK (0.135 % owf)	SAK (0.27 % owf)	SAK (0.54 % owf)
1	0.22	0.056	0.096	0.18	0.14
2	1.11	0.70	0.20	0.31	0.19
3	1.37	1.98	0.99	0.33	1.28
4	2.10	2.28	1.23	0.37	0.75
5	3.60	3.04	1.51	1.11	1.20

- Clearly, the results show that addition of Apomul SAK stabilises the fabric to
5 reduce the loss of shape which usually occurs after repeated washing.

EXAMPLE 2

- Percentage dimensional change in using Apomul SAK in combination with a
10 silicone component.

The same experimental procedure as outlined for test 1 was followed, the
treatment product being altered by the addition of a silicone component CT45E
from Wacker.

15

The % dimensional change results are given in the tables below. % dimensional
change was calculated as described above.

Cotton Interlock - % Dimensional Change

Wash Number	Water Control	SAK (0.27% owf)	15:1 by wt SAK/CT45E (0.047% owf)	10:1 by wt SAK/CT45E (0.07% owf)	5:1 by wt SAK/CT45E (0.14% owf)
1	1.97	1.21	0.43	2.64	1.40
2	12.10	3.40	0.68	1.38	0.086
3	13.83	5.65	0.75	2.51	1.29
4	29.28	7.15	0.42	1.66	0.45
5	24.36	12.27	2.02	3.70	1.47

- The results again demonstrate the improvement in dimensional stability achieved
- 5 by the use of Apomul SAK this time in combination with the silicone.

Cotton Poplin - % Dimensional Change

Wash Number	Water Control	SAK (0.27% owf)	15:1 by wt SAK/CT45E (0.047% owf)	10:1 by wt SAK/CT45E (0.07% owf)	5:1 by wt SAK/CT45E (0.14% owf)
1	0.22	0.18	0.32	0.24	0.04
2	1.11	0.31	0.17	0.47	0.14
3	1.37	0.33	0.41	0.75	0.50
4	2.10	0.37	1.16	0.56	0.41
5	3.60	1.11	0.65	1.01	0.72

- 22 -

The results again demonstrate the improvement in dimensional stability achieved by the use of Apomul SAK this time in combination with the silicone.

- 23 -

CLAIMS

1. Use of a fabric care composition comprising at least one amine- or amide-epichlorohydrin resin or derivative thereof and at least one textile compatible carrier, wherein the textile compatible carrier facilitates contact between the resin and a fabric, in a laundering process to improve fabric dimensional stability of a fabric comprising cellulosic fibres.
2. Use as claimed in Claim 1, wherein the amine or amide-epichlorohydrin resin has one or more functional groups capable of forming azetidinium groups.
3. Use according to claim 2, wherein the amine or amide-epichlorohydrin resin has one or more azetidinium functional groups.
4. Use according to claim 1 wherein the amine or amide epichlorohydrin resin or derivative thereof has one or more functional groups that contain epoxide groups or derivatives thereof.
5. Use according to any one of the preceding claims in which the composition further comprises a silicone component.
6. Use according to any one of the preceding claims wherein an amine or amide-epichlorohydrin or derivative thereof is present in the composition in an amount such that from 0.0005% to 5% by weight on weight of fabric is provided.

25

- 24 -

7. Use according to either claim 5 or claim 6, wherein the ratio of the resin to silicone component is from 1:1 to 30:1, preferably 1:1 to 20:1 and most preferably 5:1 to 15:1.
- 5 8. Use as claimed in any one of Claims 1 to 7, wherein the fabric comprises cotton or regenerated cellulose.
9. Use as claimed in any one of Claims 1 to 8, wherein the composition comprises a detergent active compound.
- 10 10. Use as claimed in any one of Claims 1 to 8, wherein the composition comprises a fabric softening and/or conditioning compound.
11. A method of treating fabric to improve its dimensional stability comprising
- 15 applying to the fabric a composition comprising at least one amine- or amide-epichlorohydrin resin or derivative thereof and a textile compatible carrier, wherein the textile compatible carrier facilitates contact between the resin and the fabric, as part of a laundering process.
- 20 12. Method as claimed in Claim 11, wherein the composition is applied to the fabric during the rinse cycle of the laundering process.

INTERNATIONAL SEARCH REPORT

Inter national Application No.

PCT/EP 99/06429

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/37 C11D3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 21715 A (PROCTER & GAMBLE) 18 July 1996 (1996-07-18) page 23, line 20 - line 31; example IV	1-4, 6, 8-12
A	GB 2 089 855 A (CIBA GEIGY AG) 30 June 1982 (1982-06-30) claims; examples	1-12
A	WO 98 29530 A (RANDALL SHERRI LYNN ; PANANDIKER RAJAN KEESHAV (US); PROCTER & GAMB) 9 July 1998 (1998-07-09) page 5, line 22 - page 7, line 4 page 11, last line - page 12, line 4 page 13, line 6 - line 14 claim 1; table 1	1

-/-

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

15 November 1999

Date of mailing of the international search report

06/12/1999

Name and mailing address of the ISA

European Patent Office, P.O. 5018 Patentkanal 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/EP 99/06429

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 393 304 A (VUILLAUME ANDRE ET AL) 28 February 1995 (1995-02-28) claim 1; example 2 -----	1,3-6, 9-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/06429

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9621715	A	18-07-1996	BR 9607483	19-05-1998
			CA 2209996	18-07-1996
			EP 0802967	29-10-1997
			FI 972969	11-07-1997
			JP 10512315	24-11-1998
			NO 973235	01-09-1997
			US 5767052	16-06-1998
GB 2089855	A	30-06-1982	AU 7859681	24-06-1982
			DE 3149680	24-06-1982
			US 4403011	06-09-1983
WO 9829530	A	09-07-1998	NONE	
US 5393304	A	28-02-1995	FR 2679573	29-01-1993
			DE 69204403	05-10-1995
			DE 69204403	01-02-1996
			EP 0530113	03-03-1993
			JP 5209349	20-08-1993
			US 5295997	22-03-1994

100 100 100 100 100 100 100 100 100 100

100 100 100 100 100 100 100 100 100 100



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C11D 3/37, 3/00	A1	(11) International Publication Number: WO 00/15748 (43) International Publication Date: 23 March 2000 (23.03.00)
<p>(21) International Application Number: PCT/EP99/06430</p> <p>(22) International Filing Date: 1 September 1999 (01.09.99)</p> <p>(30) Priority Data: 9820206.2 16 September 1998 (16.09.98) GB 9911474.6 17 May 1999 (17.05.99) GB</p> <p>(71) Applicant (for AE AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW only): UNILEVER PLC (GB/GB); Unilever House, Blackfriars, London EC4P 4BQ (GB).</p> <p>(71) Applicant (for all designated States except AE AU BB CA CY GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).</p> <p>(71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN).</p>	<p>(72) Inventors: CARSWELL, Robert, John; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). JARVIS, Anthony, Nicholas; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). KILLEY, Adelle, Louise; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). MOONEY, William; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). PARKER, Andrew, Philip; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). PECKHAM, Emily, Jane; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). SHEN, Zhengwu; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).</p> <p>(74) Agent: ELLIOTT, Peter, William; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).</p> <p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>	
<p>(54) Title: FABRIC CARE COMPOSITION</p> <p>(57) Abstract</p> <p>A fabric care composition comprises an amine or amide-epichlorohydrin resin or derivative thereof, a silicone component and, optionally, a textile compatible carrier. The textile compatible carrier facilitates contact between the resin and a fabric. The composition is adapted for use in the rinse cycle of a laundering process and may be used, as part of such a process, in the treatment of fabric to reduce creasing of the fabric.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
RJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

FABRIC CARE COMPOSITION

Technical Field

- 5 The present invention relates to fabric care compositions. In particular the invention relates to compositions applied to fabric, during the laundry process and which have a number of added benefits over and above the usual benefits from the laundry process. A method of treatment of fabric with the composition of the invention is provided and so is the use of the compositions to provide various
- 10 benefits from treatment of the fabric.

Background and Prior Art

- The laundry process generally has several benefits for fabric, the most common
- 15 being to remove dirt and stains from the fabric during the wash cycle and to soften the fabric during the rinse cycle. However, there are numerous disadvantages associated with repeated use of conventional laundry treatment compositions and/or the actual laundry process; one of these being a fairly harsh treatment of fabric in the laundry process.

- 20 Fabrics can be damaged in several ways as a result of repeated laundering and/or wear. Fabric pilling and loss of fabric surface appearance e.g. fuzzing, shrinkage (or expansion), loss of colour from the fabric or running of colour on the fabric (usually termed dye transfer) are some of the common problems associated with
- 25 repeated laundering. These problems may occur merely from repeated hand washing as well as the more vigorous machine washing process. Furthermore,

- 2 -

problems relating to damage of fabric over time through normal use, such as loss of shape and increased likelihood of wrinkling are also significant.

Laundry detergent compositions containing polyamines, optionally alkoxylated
5 are described in WO 97/42287. The detergent compositions may contain, as suds suppressors, polyorganosiloxane oils. However, there is no mention of the polyorganosiloxane oils having any function other than acting as suds suppressors. Laundry compositions containing polyamide-polyamine fabric treatment agents are described in WO 98/29530 and the detergent compositions
10 are said to impart improved overall appearance to fabrics laundered using the compositions.

WO 96/15309 and WO 96/15310 describe sprayable anti-wrinkle compositions which contain a silicone and a film-forming polymer. The compositions are
15 dispensed from a sprayer and are used as a spray treatment or as an ironing aid. However, an inherent problem with spray dispensed treatments is that they can result in localisation of the compositions in concentrated regions (so-called "spotting").

20 A process for treating fabric on an industrial scale is disclosed in EP-A-0372782. The process involves the use of an amino functional polymer and a silicone capable of reacting with reactive groupings on the amino functional polymer, the silicone generally being present in greater amounts than the amino functional polymer. The process is carried out either continuously or as a batch process and
25 is said to impart a softer handle to the fabric.

- 3 -

- US 3949014 relates to a binder for fibres which contains a polyamine-epichlorohydrin resin and an amphoteric high molecular weight compound having at least 2 cationic groups and at least 2 anionic groups per molecule. The treatment described in this document is intended to be carried out industrially as part of a fabric treatment process rather than as part of a domestic laundering process and this is supported by the fact that the fabric treated with the binder required curing at a relatively high temperature. Industrial curing of fabrics treated with this type of polymer system is normally carried out at about 150°C.
- 10 US 4371517 discloses compositions for treating fibrous materials which contain cationic and anionic polymers. The document does not deal with domestic treatments and does not relate to fabric treatment compositions containing silicones.
- 15 Co-emulsifiers, based on cationic quaternary amine polymers, are taught in DD 221922 for use in fabric softener and other compositions.

The present invention is directed towards alleviating one or more of the problems referred to hereinabove.

20

- The principal advantage of the present invention relates to reduced creasing of the fabric (compared to fabrics treated with conventional compositions) as a result of treatment with the compositions of the present invention. It will be understood that the creasing of the fabric which is reduced in the present invention is the
- 25 generally undesirable creasing of the fabric which occurs in use or during the

- 4 -

washing and/or drying of the fabric, and is usually removed by ironing or otherwise pressing the fabric, during a domestic laundering process.

5 The invention has the further advantage of increasing the dimensional stability of the fabric. The term "dimensional stability", and related terms, used herein covers not only shrinkage of fabrics but also shape retention and bagginess reduction in fabrics.

Definition of the Invention

10

The present invention relates to compositions for use in the treatment and care of fabric.

15

Thus according to one aspect of the invention there is provided a fabric care composition comprising an amine or amide-epichlorohydrin resin or derivative thereof, a silicone component and, optionally, a textile compatible carrier, wherein the textile compatible carrier facilitates contact between the resin and a fabric, the composition being adapted for use in the rinse cycle of a laundering process.

20

A second aspect of the invention relates to the use of the compositions of the invention to reduce creasing of the fabric.

25

The invention further provides a method of treating fabric in which a composition of the invention is applied to the fabric as part of a laundering process. The

- 5 -

laundering processes of the invention include the large scale and small scale (eg domestic) cleaning of fabrics.

Detailed Description of the Invention

5

The compositions of the present invention comprise, as the first component, at least one amine or amide epichlorohydrin resin or derivatives thereof.

10 In the context of the present invention these first materials are polymeric, or at least oligomeric, in nature. Preferably, they have a weight average mean molecular weight of from 300 to 1,000,000 daltons.

15 The resins of the invention are sometimes referred to below as amine-epichlorohydrin resins and polyamine-epichlorohydrin (PAE) resins (the two terms being used synonymously) although these terms encompass both the amine and amide resins of the invention. The resins may also have a mixture of amine and amide groups.

20 The amine or amide-epichlorohydrin resins may have one or more functional groups capable of forming azetidinium groups and/or one or more azetidinium functional groups.



Alternatively, or additionally the resins may have one or more functional groups that contain epoxide groups or derivatives thereof e.g. Kymene 450™ (ex Hercules).

5

Suitable polyamine-epichlorohydrin (PAE) resins include those described in 'Wet Strength Resins and Their Application', pp 16-36, ed. L.L.Chan, Tappi Press, Atlanta, 1994. Suitable PAE resins can be identified by selecting those resins which impart increased wet strength to paper, after treatment, in a relatively
10 simple test.

Any amine or amide-epichlorohydrin resin having an epoxide functional group or derivative thereof is suitable for use according to the invention.

- 15 A particularly preferred class of amine or amide-epichlorohydrin resins for use in the invention are secondary amine or amide-based azetidinium resins, for example, those resins derived from a polyalkylene polyamine e.g. diethylenetriamine (DETA), a polycarboxylic acid e.g. adipic acid or other dicarboxylic acids, and epichlorohydrin. Other polyamines or polyamides can
20 also be advantageously used in the preparation of suitable PAE resins.

Another preferred class of amine-epichlorohydrin resins for use in the invention are those having an epoxide functional group of derivative thereof e.g. chlorohydrin.

25

- 7 -

The resin is preferably present in the product in a sufficient quantity to give an amount of 0.0005 % to 5 % by weight on the fabric based on the weight of the fabric, more preferably 0.001 % to 2 % by weight on fabric. The amount of the first component in the composition required to achieve the above % by weight on
5 fabric will typically be in the range 0.01% to 35% by weight, preferably 0.1 % to 13.5 % by weight.

The resin may be PDAA-epichlorohydrin resins or PMDAA-epichlorohydrin resins. PDAA is poly(diallylamine) and PMDAA is poly(methyldiallyl(amine)).
10

The compositions of the invention, when applied to a fabric, can impart benefits to the fabric when uncured. However, they may be cured by a domestic curing step including ironing and/or domestic tumble drying, preferably tumble drying. The curing is preferably carried out at a temperature in the range of from 50 to
15 100°C, more preferably from 80 to 100°C.

The compositions of the invention comprise a silicone component. It is preferred if the silicone component is a dimethylpolysiloxane with amino alkyl groups. It may be used in the context of the present invention as an emulsion in water.
20

It is preferred if the silicone component is present in a ratio of first component: silicone of from 1:1 to 30:1, more preferably 1:1 to 20:1 (eg, 2:1 to 20:1) and most preferably 5:1 to 15:1.

25 In the context of the present invention the term 'textile compatible carrier' is a component which can assist in the interaction of the first component with the

fabric. The carrier can also provide benefits in addition to those provided by the first component e.g. softening, cleaning etc. The carrier may be water or a detergent-active compound or a fabric softener or conditioning compound or other suitable detergent or fabric treatment agent.

5

The compositions of the invention are adapted to be used in the rinse cycle of a laundry process as part of a conventional fabric treatment product and may be packaged and labelled as such. Preferably the rinse cycle follows treatment of the fabric with a detergent. The laundry process is preferably a domestic laundering process.

10

The fabrics which may be treated in the present invention comprise cellulosic fibres, preferably from 1% to 100% cellulosic fibres (more preferably 5% to 100% cellulosic fibres, most preferably 40% to 100% such as 75% to 100%).

15

When the fabric contains less than 100% cellulosic fibres, the balance comprises other fibres or blends of fibres suitable for use in garments such as polyester, for example. Preferably, the cellulosic fibres are of cotton or regenerated cellulose such as viscose.

20

The composition may be a rinse adjunct, in which case it may contain only water, the PAE resin and the silicone component. However, the composition preferably comprises also a perfume agent, and, optionally, other conventional additives in rinse adjuncts.

- 9 -

If the composition of the invention is a rinse conditioner, it will preferably comprise a textile-compatible carrier which is a fabric softening and/or conditioning compound.

5 Fabric Softening and/or Conditioner Compounds

If the composition of the present invention is in the form of a fabric conditioner composition, the textile-compatible carrier will be a fabric softening and/or conditioning compound (hereinafter referred to as "fabric softening compound"),
10 which may be a cationic or nonionic compound.

The softening and/or conditioning compounds may be water insoluble quaternary ammonium compounds. The compounds may be present in amounts of up to 8% by weight (based on the total amount of the composition) in which case the
15 compositions are considered dilute, or at levels from 8% to about 50% by weight, in which case the compositions are considered concentrates.

Compositions suitable for delivery during the rinse cycle may also be delivered to the fabric in the tumble dryer if used in a suitable form. Thus, another product
20 form is a composition (for example, a paste) suitable for coating onto, and delivery from, a substrate e.g. a flexible sheet or sponge or a suitable dispenser during a tumble dryer cycle.

Suitable cationic fabric softening compounds are substantially water-insoluble
25 quaternary ammonium materials comprising a single alkyl or alkenyl long chain having an average chain length greater than or equal to C_{20} or, more preferably, compounds comprising a polar head group and two alkyl or alkenyl chains having

- 10 -

an average chain length greater than or equal to C_{14} . Preferably the fabric softening compounds have two long chain alkyl or alkenyl chains each having an average chain length greater than or equal to C_{16} . Most preferably at least 50% of the long chain alkyl or alkenyl groups have a chain length of C_{18} or above. It is preferred if the long chain alkyl or alkenyl groups of the fabric softening compound are predominantly linear.

Quaternary ammonium compounds having two long-chain aliphatic groups, for example, distearyldimethyl ammonium chloride and di(hardened tallow alkyl) dimethyl ammonium chloride, are widely used in commercially available rinse conditioner compositions. Other examples of these cationic compounds are to be found in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. Any of the conventional types of such compounds may be used in the compositions of the present invention.

The fabric softening compounds are preferably compounds that provide excellent softening, and are characterised by a chain melting $L\beta$ to $L\alpha$ transition temperature greater than 25°C , preferably greater than 35°C , most preferably greater than 45°C . This $L\beta$ to $L\alpha$ transition can be measured by DSC as defined in "Handbook of Lipid Bilayers", D Marsh, CRC Press, Boca Raton, Florida, 1990 (pages 137 and 337).

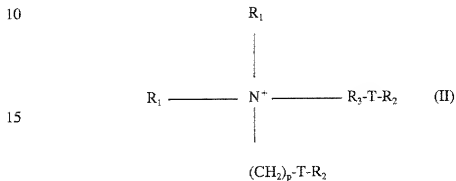
Substantially water-insoluble fabric softening compounds are defined as fabric softening compounds having a solubility of less than 1×10^{-3} wt % in demineralised water at 20°C . Preferably the fabric softening compounds have a

- 11 -

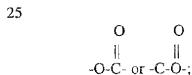
solubility of less than 1×10^{-4} wt%, more preferably less than 1×10^{-8} to 1×10^{-6} wt%.

Especially preferred are cationic fabric softening compounds that are water-

- 5 insoluble quaternary ammonium materials having two C_{12-22} alkyl or alkenyl groups connected to the molecule via at least one ester link, preferably two ester links. An especially preferred ester-linked quaternary ammonium material can be represented by the formula II:



- 20 wherein each R_1 group is independently selected from C_{1-4} alkyl or hydroxyalkyl groups or C_{2-4} alkenyl groups; each R_2 group is independently selected from C_{8-28} alkyl or alkenyl groups; and wherein $-R_3-$ is a linear or branched alkylene group of 1 to 5 carbon atoms, T is

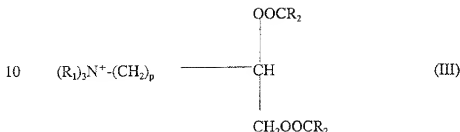


- 30 and p is 0 or is an integer from 1 to 5.

- 12 -

Di(tallowoxyloxyethyl) dimethyl ammonium chloride and/or its hardened tallow analogue is especially preferred of the compounds of formula (II).

A second preferred type of quaternary ammonium material can be represented by
 5 the formula (III):



15 wherein R_1 , p and R_2 are as defined above.

It is advantageous if the quaternary ammonium material is biologically biodegradable.

20 Preferred materials of this class such as 1,2-bis(hardened tallowoyloxy)-3-trimethylammonium propane chloride and their methods of preparation are, for example, described in US 4 137 180 (Lever Brothers Co). Preferably these materials comprise small amounts of the corresponding monoester as described in US 4 137 180, for example, 1-hardened tallowoyloxy-2-hydroxy-3-
 25 trimethylammonium propane chloride.

Other useful cationic softening agents are alkyl pyridinium salts and substituted imidazoline species. Also useful are primary, secondary and tertiary amines and the condensation products of fatty acids with alkylpolyamines.

The compositions may alternatively or additionally contain water-soluble cationic fabric softeners, as described in GB 2 039 556B (Unilever).

- 5 The compositions may comprise a cationic fabric softening compound and an oil, for example as disclosed in EP-A-0829531.

The compositions may alternatively or additionally contain nonionic fabric softening agents such as lanolin and derivatives thereof.

10

Lecithins are also suitable softening compounds.

- Nonionic softeners include L β phase forming sugar esters (as described in M Hato et al Langmuir 12, 1659, 1666, (1996)) and related materials such as
15 glycerol monostearate or sorbitan esters. Often these materials are used in conjunction with cationic materials to assist deposition (see, for example, GB 2 202 244. Silicones are used in a similar way as a co-softener with a cationic softener in rinse treatments (see, for example, GB 1 549 180).

- 20 The compositions may also suitably contain a nonionic stabilising agent. Suitable nonionic stabilising agents are linear C₈ to C₂₂ alcohols alkoxylated with 10 to 20 moles of alkylene oxide, C₁₀ to C₂₀ alcohols, or mixtures thereof. Advantageously the nonionic stabilising agent is a linear C₈ to C₂₂ alcohol alkoxylated with 10 to 20 moles of alkylene oxide. Preferably, the level of
25 nonionic stabiliser is within the range from 0.1 to 10% by weight, more preferably from 0.5 to 5% by weight, most preferably from 1 to 4% by weight. The mole ratio of the quaternary ammonium compound and/or other cationic

- 14 -

softening agent to the nonionic stabilising agent is suitably within the range from 40:1 to about 1:1, preferably within the range from 18:1 to about 3:1.

- The composition can also contain fatty acids, for example C_8 to C_{24} alkyl or alkenyl monocarboxylic acids or polymers thereof. Preferably saturated fatty acids are used, in particular, hardened tallow C_{16} to C_{18} fatty acids. Preferably the fatty acid is non-saponified, more preferably the fatty acid is free, for example oleic acid, lauric acid or tallow fatty acid. The level of fatty acid material is preferably more than 0.1% by weight, more preferably more than 0.2% by weight. Concentrated compositions may comprise from 0.5 to 20% by weight of fatty acid, more preferably 1% to 10% by weight. The weight ratio of quaternary ammonium material or other cationic softening agent to fatty acid material is preferably from 10:1 to 1:10.
- 15 The fabric conditioning compositions include silicones, such as predominantly linear polydialkylsiloxanes, e.g. polydimethylsiloxanes or aminosilicones containing amine-functionalised side chains; and may also include soil release polymers such as block copolymers of polyethylene oxide and terephthalate; amphoteric surfactants; smectite type inorganic clays; zwitterionic quaternary ammonium compounds; and nonionic surfactants.
- 20

- The fabric conditioning compositions may also include an agent which produces a pearlescent appearance, e.g. an organic pearlising compound such as ethylene glycol distearate, or inorganic pearlising pigments such as microfine mica or titanium dioxide (TiO_2) coated mica.
- 25

- 15 -

The fabric conditioning compositions may be in the form of emulsions or emulsion precursors thereof.

Other optional ingredients include emulsifiers, electrolytes (for example, sodium chloride or calcium chloride) preferably in the range from 0.01 to 5% by weight, pH buffering agents, and perfumes (preferably from 0.1 to 5% by weight).

Further optional ingredients include non-aqueous solvents, perfume carriers, fluorescers, colourants, hydrotropes, antifoaming agents, antiredeposition agents, enzymes, optical brightening agents, opacifiers, anti-shrinking agents, anti-wrinkle agents, anti-spotting agents, dye transfer inhibitors, germicides, fungicides, anti-oxidants, UV absorbers (sunscreens), heavy metal sequestrants, chlorine scavengers, dye fixatives, anti-corrosion agents, drape imparting agents, antistatic agents and ironing aids. This list is not intended to be exhaustive.

The invention will now be described by way of example only and with reference to the following non-limiting examples.

EXAMPLES

EXAMPLES 1-3

Experimental Procedure

The amine epichlorohydrin resin used in the following tests is Apomul SAK, (ex. Brookstone Chemicals) which has an azetidinium functional group. It was

- 16 -

prepared as an aqueous solution and utilised as a percentage of the weight of fabric treated (% on weight of fabric (owf)) to show its effect on fabric dimensional stability.

- 5 Two types of fabric, cotton interlock and cotton poplin, were used in the procedure below. Each fabric was tested in the weft and warp direction, figures relating to the % dimensional change (by multiplying the % change in the weft direction by the % change in the warp direction) have been tabulated.
- 10 All fabrics pieces were pre-washed prior to treating (40°C cotton wash in a Miele Novotronic W820 Front Loading Washing Machine, Wirral water, 100g Persil non biological washing powder, then tumble dried in a Miele Novotronic T430 Tumble Dryer). The fabrics pieces were then marked up using the M&S Shrinkage Rule and labelled. Four pieces of each fabric type plus clean cotton
- 15 sheeting made up a 2.5kg load, which was washed (40°C cotton wash in a Miele Novotronic W820 Front Loading Washing Machine, Wirral water, 100g Persil non biological washing powder added in the main wash. Apomul SAK was added in the final rinse), then tumble dried in a Miele Novotronic T430 Tumble Dryer, and finally lightly ironed on both sides (cotton setting). Ironing only took place
- 20 after the first wash. The fabric pieces were then conditioned for 24 hours at 65% RH, 20°C. The washing and drying stages were repeated until five washes were completed.

- For determining the percentage dimensional change in using Apomul SAK in
- 25 combination with a silicone component, the same experimental procedure as

- 17 -

outlined above was followed, the treatment product being altered by the addition of a silicone component CT45E from Wacker.

- The % dimensional change results are given in the tables below. % dimensional change was calculated the mean warp % values by the mean weft % values ie, the mean value is calculated from the values obtained before and after each such test.

Cotton Interlock - % Dimensional Change

			EXAMPLE 1	EXAMPLE 2	EXAMPLE 3
Wash Number	Water Control	SAK (0.27 % owf)	15:1 by wt SAK/CT45E (0.047 % owf)	10:1 by wt SAK/CT45E (0.07 % owf)	5:1 by wt SAK/CT45E (0.14 % owf)
1	1.97	1.21	0.43	2.64	1.40
2	12.10	3.40	0.68	1.38	0.086
3	13.83	5.65	0.75	2.51	1.29
4	29.28	7.15	0.42	1.66	0.45
5	24.36	12.27	2.02	3.70	1.47

10

The results demonstrate the improvement in dimensional stability achieved by the use of Apomul SAK in combination with the silicone.

Cotton Poplin - % Dimensional Change

Wash Number	Water Control	SAK (0.27% owf)	15:1 by wt SAK/CT45E (0.047% owf)	10:1 by wt SAK/CT45E (0.07% owf)	5:1 by wt SAK/CT45E (0.14% owf)
1	0.22	0.18	0.32	0.24	0.04
2	1.11	0.31	0.17	0.47	0.14
3	1.37	0.33	0.41	0.75	0.50
4	2.10	0.37	1.16	0.56	0.41
5	3.60	1.11	0.65	1.01	0.72

- The results again demonstrate the improvement in dimensional stability achieved by the use of Apomul SAK™ in combination with the silicone.

EXAMPLE 4

- Each load consisted of ten 45 cm x 45 cm pieces of cotton sheeting, six 45 cm x 45 cm pieces of 50:50 polycotton, five 45 cm x 45 cm interlock and the load made up to 1 kg using cotton sheeting ballast. The experiments were done in duplicate with each load being combined for tumble drying. Each load was washed in a Miele® machine using a 40°C economy wash and either no additive to the rinse (untreated), CT 45E silicone polymer from Wacker (0.5% owf) or a composition according to the invention containing a PAE (0.32% owf) (Apomul SAK™) and CT45E (0.18% owf). After tumble drying in a Miele® machine on normal setting until the anti-crease finish had been obtained, the cotton sheeting

- 19 -

samples were panelled against standards (-the best two and worst two samples were removed prior to panelling).

- The results of the panel testing on a scale of 0 for no creasing to 100 for maximum creasing are as follows:

Treatment	Average Score
Untreated	68.73
CT45E	77.06
PAE/CT45E	57.62

EXAMPLE 5

- 10 The previous example was repeated using loads consisting of ten 40 cm x 40 cm pieces of cotton sheeting, six 40 cm x 40 cm pieces of 50:50 polycotton, five 40cm x 40 cm pieces of interlock and the load made up to 1 kg using cotton sheeting ballast. The additives added to the rinse were none (untreated), Comfort® fabric conditioner (0.25% owf) or the composition according to the
- 15 invention as used in the previous example. The loads were varied in each machine ensuring that after 5 loads each treatment had been in the same number of machines. After each wash the loads were combined and dried in a Miele® tumble dryer on normal setting until the anti-crease finish had been obtained. The cotton sheeting samples were panel tested after the fifth wash.

- 20 -

The results are as follows:

Treatment	Average Score
Untreated	74.21
Comfort®	50.24
PAE/CT45E	37.54

5 EXAMPLE 6

Three sets of eight different garments purchased from a Marks & Spencer store were washed five times in a Miele® washing machine on cotton programme at 40°C.

10

The garments were:

- i. Mid green men's heavy cotton drill shirt, 100% cotton
- ii. Children's Rugrats™ pyjamas, 100% cotton
- 15 iii. Mid blue men's shirt, 65:35 polycotton
- iv. Light blue men's shirt, 65:35 polycotton
- v. Dark blue 'easy care' men's shirt, 45:55 polycotton
- vi. Camouflage boys teeshirt, 100% cotton
- vii. Navy blue jeans, 98% cotton 2% elastane
- 20 viii. Navy, royal and white striped men's rugby shirt, 100% cotton

- 21 -

All three sets of garments were washed with 65 g Persil® detergent with rinse treatments containing no additive (untreated), 21g Comfort ® fabric conditioner (Comfort) or a composition according to the invention (invention) containing 27.1 g PAE (Apomul SAK™) and 5.9 g CT45E.

5

After washing, the garments were panelled by 20 people. Each person was asked to compare the untreated, comfort and invention garments from each set and to carry out the following assessments:

- 10
1. Rank the garments in terms of creasing.
 2. State which garments need ironing.
 3. State which garment has the best overall appearance.
 4. State which garment has the best feel.
 5. State which garment has the best feel and appearance.

15

The crease ranking was carried out by giving each garment a score of 1, 2 or 3, with 1 being least creased and 3 the most creased.

- For the ironing assessment, a score of 1 was given to indicate that ironing is
- 20 required and a score of 0 indicated that no ironing is required.

- 22 -

The results are given below:

Garment	Treatment	Crease Ranking	Ironing Requirement	Overall Appearance	Feel	Feel/Overall Appearance
Mid-blue shirt	Untreated	2.65	0.85	0.10	0	0.05
	Comfort	1.95	0.7	0.15	0.10	0.10
	Invention	1.45	0.35	0.75	0.85	0.80
Light blue shirt	Untreated	2.60	1.00	0.10	0	0.05
	Comfort	1.45	0.70	0.65	0.45	0.65
	Invention	1.90	0.80	0.25	0.75	0.30
Rugby Shirt	Untreated	2.70	0.75	0.05	0	0
	Comfort	2.40	0.55	0.10	0	0.05
	Invention	1.10	0.15	0.85	0.95	0.95
Jeans	Untreated	3.00	1.00	0	0	0
	Comfort	1.90	0.25	0.15	0.25	0.10
	Invention	1.05	0.10	0.85	0.80	0.90
Dark blue shirt	Untreated	2.95	1.00	0.05	0	0
	Comfort	1.40	0.20	0.55	0.25	0.35
	Invention	1.55	0.20	0.40	0.75	0.60
Childs pyjamas	Untreated	2.95	0.85	0.15	0	0
	Comfort	1.90	0.20	0.05	0.30	0.25
	Invention	1.10	0.05	0.75	0.75	0.85
Dark green shirt	Untreated	3.00	1.00	0	0.05	0
	Comfort	1.75	0.85	0	0.25	0.10
	Invention	1.15	0.55	0.90	0.80	0.85
Camou-flage T-Shirt	Untreated	2.70	0.90	0	0	0
	Comfort	2.25	0.75	0.10	0.10	0.10
	Invention	1.05	0.10	0.90	0.95	0.90

EXAMPLES 7 A-E

5

Tests were carried out on the crease recovery angle (CRA) of a fabric (100% cotton sheeting; undyed, unfinished, non-mercerised) with compositions 7A-E according to the invention padded onto 50 mm x 25 mm pieces of the fabric (6 pieces in the warp direction and 6 pieces in the weft direction) at levels of about

- 23 -

- 6.5% owf and at a pH of about 7.5. The ratio of silicone to PAE was varied to demonstrate the synergistic effect of using PAE and silicone together. CRA was measured by conditioning the pieces for 24 hours at 20°C, 65% RH. The samples were folded in half and placed under a 1 kg load for 60 seconds. The
- 5 fabric piece was then placed into a CRA protractor and the fold angle measured after 60 seconds recovery. The average warp and weft values were combined to give an overall CRA value.

Treatment	PAE ^a (%)	Silicone ^b (%)	Resin owf (%)	Average CRA ^c (°)
None (control)	0	0	0	135.33
Silicone	0	100	6.6	214.90
7A	10	90	6.6	232.53
7B	25	75	6.6	232.17
7C	50	50	6.4	228.33
7D	75	25	6.1	228.33
7E	90	10	6.2	204.00
PAE	100	0	5.48	173.33

- 10 All percentages are by weight

^aApomul SAK

^bCT45E aminosilicone (Wacker)

^cWarp + weft average values

15 EXAMPLE 8 A-G

The following are examples of compositions according to the invention which have been formulated for use as adjuncts in the rinse cycle of a domestic laundering process.

- 24 -

Example	PAE ^a (%)	Silicone ^b (%)	Perfume ^c (%)	Ratio PAE:Silicone
8A	69.9	29.6	0.5	1:2
8B	82.1	17.4	0.5	1:1
8C	88.9	10.6	0.5	1.78:1
8D	90.0	9.5	0.5	2:1
8E	88.9	10.6	0.5	1.78:1
8F	88.9	10.6	0.5	1.78:1
8G	88.9	10.6	0.5	1.78:1

All percentages are by weight

^aKenores 1440 (13.5% active)

^bCT45E (Wacker) aminosilicone

5 ^cExamples A-D - Dandi Lion (IFF)

Example E - Lilial

Example F - Limonene

Example G - Citronellol

CLAIMS

1. Fabric care composition comprising an amine or amide-epichlorohydrin resin or derivative thereof, a silicone component and, optionally, a textile
5 compatible carrier, wherein the textile compatible carrier facilitates contact between the resin and a fabric, the composition being adapted for use in the rinse cycle of a laundering process.
2. Fabric care composition as claimed in Claim 1 wherein the textile
10 compatible carrier is a fabric softening and/or conditioning compound.
3. Fabric care composition as claimed in Claim 1 or Claim 2, wherein the amine or amide-epichlorohydrin resin has one or more functional groups capable of forming azetidinium groups.
15
4. Fabric care composition as claimed in Claim 3, wherein the amine or amide-epichlorohydrin resin has one or more azetidinium functional groups.
5. Fabric care composition as claimed in Claim 1 or Claim 2, wherein the
20 amine or amide-epichlorohydrin resin or derivative thereof has 1 or more functional groups that contain epoxide groups or derivatives thereof.
6. Fabric care composition according to any preceding claim wherein an amine or amide-epichlorohydrin resin or derivative thereof is present in the
25 composition in an amount such that from 0.0005 % to 5 % by weight on weight of fabric is provided.

- 26 -

7. Fabric care composition according to Claim 6, wherein the ratio of the resin to silicone component is from 1:1 to 30:1, preferably 1:1 to 20:1 and most preferably 5:1 to 15:1.

5

8. Fabric care composition according to any preceding claim wherein the silicone comprises at least one aminoalkyl group.

9. Use of a fabric care composition as defined in any one of Claims 1 to 8 in
10 the treatment of fabric to reduce creasing of the fabric.

10. A method of treating fabric comprising the step of applying to fabric a fabric care composition as defined in any one of claims 1 to 8 as part of a laundering process.

15

11. Method as claimed in Claim 10, wherein the fabric comprises a cellulosic fibre.

12. Method as claimed in Claim 11, wherein the cellulosic fibre is cotton or
20 regenerated cellulose.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 99/06430

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/37 C11D3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 21715 A (PROCTER & GAMBLE) 18 July 1996 (1996-07-18) page 23, line 20 - line 31; example IV ---	1-6, 9-12
A	GB 2 089 855 A (CIBA GEIGY AG) 30 June 1982 (1982-06-30) claims; examples ---	1
A	US 4 735 738 A (WILLMAN KENNETH W) 5 April 1988 (1988-04-05) examples I, IX-XII column 10, line 9 - column 11, line 20 --- -/-	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
 "&" document member of the same patent family

Date of the actual completion of the international search

12 November 1999

Date of mailing of the international search report

06/12/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentstrasse 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax. (+31-70) 340-3016

Authorized officer

Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/06430

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 29530 A (RANDALL SHERRI LYNN ;PANANDIKER RAJAN KEESHAV (US); PROCTER & GAMB) 9 July 1998 (1998-07-09) page 5, line 22 -page 7, line 4 page 11, last line -page 12, line 4 page 13, line 6 - line 14 claim 1; table 1 -----	1
A	US 5 393 304 A (VUILLAUME ANDRE ET AL) 28 February 1995 (1995-02-28) claim 1; example 2 -----	1,3-6, 9-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/06430

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9621715	A	18-07-1996	BR 9607483 A	19-05-1998
			CA 2209996 A	18-07-1996
			EP 0802967 A	29-10-1997
			FI 972969 A	11-07-1997
			JP 10512315 T	24-11-1998
			NO 973235 A	01-09-1997
			US 5767052 A	16-06-1998
GB 2089855	A	30-06-1982	AU 7859681 A	24-06-1982
			DE 3149680 A	24-06-1982
			US 4403011 A	06-09-1983
US 4735738	A	05-04-1988	AU 584047 B	11-05-1989
			AU 6420286 A	30-04-1987
			CA 1263901 A	19-12-1989
			DE 3688315 A	27-05-1993
			EP 0220904 A	06-05-1987
			JP 8022355 B	06-03-1996
			JP 62162080 A	17-07-1987
			NZ 218007 A	26-06-1990
WO 9829530	A	09-07-1998	NONE	
US 5393304	A	28-02-1995	FR 2679573 A	29-01-1993
			DE 69204403 D	05-10-1995
			DE 69204403 T	01-02-1996
			EP 0530113 A	03-03-1993
			JP 5209349 A	20-08-1993
			US 5295997 A	22-03-1994

